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FINAL REPORT  
(April 10, 1980 through July 31, 1981)

on

ULTRAPURE GLASS OPTICAL WAVEGUIDE  
DEVELOPMENT IN MICROGRAVITY  
BY THE SOL-GEL PROCESS  
(JPL CONTRACT 955710)

to

JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY

January 15, 1982

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by

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#### INTRODUCTION

The melting of glass in a terrestrial environment involves an obstacle to maintaining high purity levels due to contamination by container walls, a problem which can be alleviated by containerless melting in the space environment. The ultimate objective of the present research program is to take advantage of the containerless melting of glasses in space for the preparation of ultrapure homogeneous glass for optical waveguides. However, the homogenization of the glass using conventional raw materials is normally achieved on earth either by the gravity induced convection currents or by the mechanical stirring of the melt. Because of the absence of gravity induced convection currents, the homogenization of glass using conventional raw materials will be difficult in the space environment.

Multicomponent, homogeneous, noncrystalline oxide gels can be prepared by the sol-gel process and these gels are promising starting materials for melting glasses in the space environment. The sol-gel process referred to here is based on the polymerization reaction of alkoxy-silane with other metal alkoxy compounds or suitable metal salts. Many of the alkoxy-silanes or other metal alkoxides are liquids and thus can be



purified by distillation. The use of gels offers several advantages such as high purity and lower melting times and temperatures. Hence, the present research program aims at the utilization of the sol-gel process for the preparation of multicomponent, ultrapure glass batches for subsequent containerless melting of the batches in space to prepare glass blanks for optical waveguides.

Prior to "space readiness", however, several critical control points must be carefully evaluated on earth. Hence the present ground based program comprises two major phases; Phase 1 and Phase 2.

Phase 1 involves the following activities:

- Selection of the best multicomponent glass system suitable for optical waveguides.
- Choice of composition in a particular system.
- Preparation of gels in the chosen multicomponent system (with reagent grade chemicals) by different procedures.
- Thermal treatment of gels for removal of volatiles and water.
- Characterization of gels.
- Melting of gels prepared by different procedures.
- Characterization of the resulting glasses in terms of properties relevant to optical waveguide applications.

Phase 2, to be initiated in a follow-on effort, plans to concentrate on the following activities:

- Preparation of ultrapure gels by using ultrapure chemicals and a Class 100 clean room.
- Melting of ultrapure gel pellets using both a container and containerless melting.
- Characterization of glasses in terms of trace level transition metal impurities and absorptive losses.

Some of the activities of Phase 1 were performed during 1979 (JPL Contract 955361) and have been reported in the Final Report

to Jet Propulsion Laboratory, dated February 22, 1980. Further Phase 1 activities were performed in 1980 and are summarized in an Interim Report dated January 15, 1981. The latter work consisted of the following activities:

- (a) Preparation of gels in the alkali borosilicate system by different procedures developed during the initial period of the program.
- (b) Evaluation of the physico-chemical nature of gels prepared by different procedures.
- (c) Investigations of the structure of glasses obtained by the melting of gels prepared by different procedures.
- (d) Effects of the melting history (e.g., time and temperature) on the structure of glasses obtained from gels.
- (e) Thermal treatment for the removal of hydroxyl groups from gels.

In this Final Report, Phase 1 has been completed and represents work carried out through July 31, 1981. In this period, emphasis was placed on gel preparation procedures and compositions to show that the physico-chemical nature of the gels are strongly influenced by the process parameters.

#### SUMMARY

Our primary objective is the utilization of the sol-gel process for the preparation of multicomponent, ultrapure glass batches for subsequent containerless melting to prepare glass blanks for optical waveguides. The objectives of the completed first phase of the work were as follows:

- Selection of a multicomponent glass system for optical waveguide applications.
- Development of gel preparation procedures for the chosen multicomponent system (with reagent grade chemicals).

- Thermal treatment of gels for removal of volatiles and water.
- Characterization of gels.
- Melting of gels prepared by different procedures.
- Determination of water content of the resulting glasses.
- Rayleigh scattering studies of the glasses prepared by the melting of different gels.
- Comparison of the microstructures of the phase separated glasses obtained from the gels prepared by two different procedures.

The glass system chosen in the first task of the program was the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system. The intrinsic attenuation of the glass was originally of interest in the visible and near infrared region (0.80 to 0.9  $\mu\text{m}$ ) of wavelength. The alkaliborosilicate system was acceptable in this first operating wavelength region. This glass system was investigated for optical waveguide applications.<sup>(1)</sup> Consequently, some properties of this system relevant to the optical waveguide application were available. So, the soda borosilicate system is an ideal system for the development and understanding of the gel preparation procedures and also for the characterization of the gel-derived glasses because the physico-chemical properties and structures of the glasses in this system are available in the literature.

The results of this research project completed in July, 1981, can be summarized as follows:

Gels of different compositions in the sodium borosilicate system were prepared by three different procedures using three different sources of  $\text{Na}_2\text{O}$ . The influence of various process parameters (such as chemical nature of the reactants, the pH of the medium, the concentration of water and the reactants) on the gelling process were investigated. The results show that the physico-chemical nature of gels and gel-monoliths are strongly influenced by the process parameters.

The removal of organics for the gel powders were related to the gel preparation procedures and the compositions of the gels. The different

time and temperature required for the removal of organics from the different gels might be explained in terms of entrapping of the residual organics in the pores which would depend on the nature of the porosity and the rate of closing of the pore during the thermal treatment cycle. The difference in the physico-chemical nature of the gels could be explained in terms of the anticipated mechanics and kinetics of the gelling processes that take place under the experimental conditions in each procedure used. Infrared absorption spectra of the gels prepared by the different procedures indicate some finite differences in the molecular structure of the gels. However, the melting of gels at higher temperatures ( $>1200$  C) results in near equilibrium in the melts for each of the gels. The microstructures of the phase separated glasses obtained from the gels prepared by the different procedures were found to be different. Most likely, the difference is due to the presence of different concentration of hydroxyl groups which influence the phase separation. The hydroxyl groups from the porous gel powders were reduced to a great extent by passing dry oxygen or reactive gases through the porous gels at temperatures below the closing of the pores. The hydroxyl content of glasses obtained by the melting of gels prepared by the different procedures were also found to be different. Further removal of hydroxyl groups was achieved by bubbling dry  $N_2$  through the glass during melting. The hydroxyl content of the glasses after bubbling with dry  $N_2$  was in the range of 10 to 20 ppm. No further systematic investigation was carried out to get a minimum value. It may be noted that the proper choice of temperature, time, and reactive gas during the chemical treatment of the gel powders would further reduce the hydroxyl content of the glass. The glass composition we used contained a high concentration of  $B_2O_3$ , and consequently, it required highly controlled experimental conditions for the further reduction of hydroxyl groups from these glasses. Rayleigh scattering studies of the glasses obtained from the gels prepared by different procedures were made. The results of these Rayleigh scattering measurements indicate that the homogeneity of gel-derived glasses is much higher than that of the glass prepared by the conventional technique. The results also indicate that there is a difference in homogeneity of the glasses prepared by different gel preparation procedures.

## PART IA. GENERAL EXPERIMENTAL PROCEDURES FOR GEL-DERIVED GLASSES

The experimental procedures of the present work have been divided into the following activities:

- Choice of composition.
- Preparation of gels.
- Thermal treatment of gels.
- Characterization of gels.
- Conversion of gels to glasses by melting.
- Characterization of glasses.

### Choice of Composition

The objective of the initial work was to establish the procedures required to prepare multicomponent glasses via the gel route and evaluate phenomena likely to be important in melting and characterization of glasses. Three different compositions were chosen to study the various aspects of the present investigation. The compositions are given in Table 1.

Composition 1 lies outside the metastable liquid-liquid immiscibility zone of the ternary  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system. It was selected to establish the gel preparation procedures and to investigate the removal of hydroxyl groups from the gels before melting, and subsequently from the glass during melting. Moreover, it was presumed that the preparation of gels with such high alkali content would encounter more difficulties associated with non-uniform distribution of  $\text{Na}^+$  ions.

Composition 2 was chosen for preparing glasses for the Rayleigh Scattering studies. This composition was chosen because some previous work<sup>(2)</sup> on Rayleigh Scattering has been done with this composition prepared by conventional methods and, as such, it would be possible to compare the results of the gel-derived glasses with those of the conventional glasses.

TABLE 1. COMPOSITION OF GLASSES

Composition No.	(Weight Percent)		
	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O
1	60.0	15.0	25.0
2	55.0	25.0	20.0
3	60.0	30.0	10.0

Composition 3 which falls within the liquid-liquid immiscibility zone in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system was chosen to study the phase separation behavior of gel-derived glasses.

The locations of the above compositions in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  ternary diagram is shown in Figure 1.

### Preparation of Gels

The development of the gel preparation procedures has been considered in terms of several factors which are important for fulfilling the objectives of the present research program. The following factors have been considered.

- Chemical nature of the starting compounds and the purity attainable with the starting compounds.
- Homogeneity of the multicomponent solution and the gelling process.
- Removal of volatile organic or inorganic compounds by thermal treatment.
- Crystallinity of gels.

### Starting Compounds

The following starting compounds have been used as sources of different oxides in the different procedures.

<u>Oxide</u>	<u>Source</u>
$\text{SiO}_2$	Tetraethyl Orthosilicate
$\text{B}_2\text{O}_3$	Boric Acid
	Trimethyl Borate
$\text{Na}_2\text{O}$	Sodium Methylate
	Sodium Nitrate
	Sodium Acetate

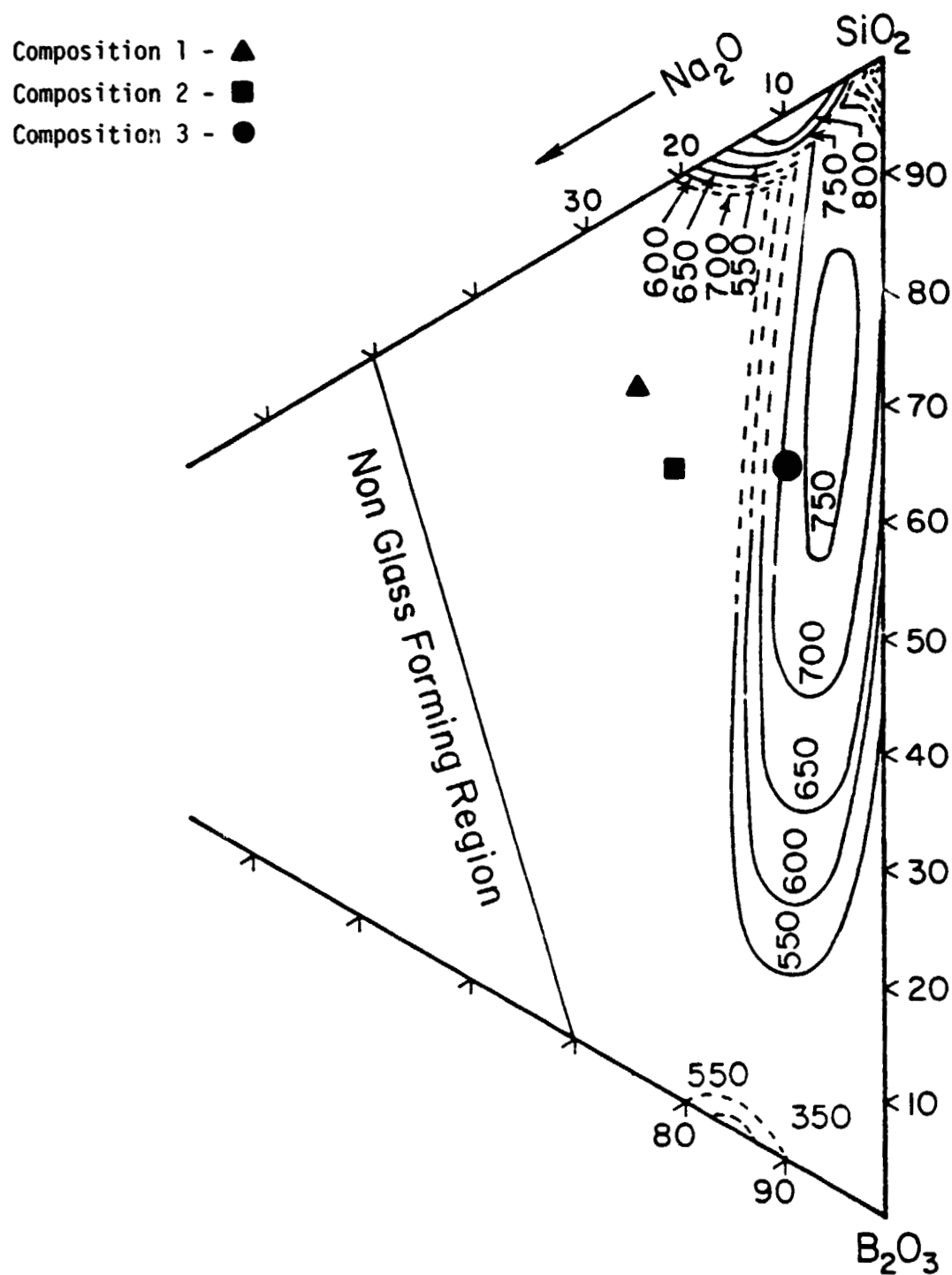


FIGURE 1. Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> TERNARY DIAGRAM SHOWING THE PROJECTION OF THE IMMISCIBILITY SURFACE AT DIFFERENT TEMPERATURES



Note that the compounds that are commercially available in ultrapure conditions are:

Tetraethyl Silicate

Boric Acid

Sodium Nitrate

Though trimethyl borate is not available on the market it can be, in principle, purified to ultrapure condition by distillation.

#### Homogeneity of the Solution and the Gelling Process

Since the homogeneity of gels in terms of cation distribution is an important objective of the present work, the preparation procedures have been critically judged in terms of homogeneity. Thus, the stability of the solution on addition of different constituents and the homogeneity that could be achieved were considered.

The homogeneity and the stability of the solution are influenced by various process parameters such as the nature of the reactants, the pH of the medium, the concentration of the reactants, and the presence of minor additives. A qualitative assessment of the above factors have been made.

#### Removal of Organic Groups

The removal of residual organic groups from the gel by the low temperature (<500 C) thermal treatments is a complex process and appears to be also related to the gel preparation procedures. The primary concerns were to prevent carbonization during the thermal treatments, and to have an understanding of the relation between the gel preparation process and the removal processing of the organic groups.

### Crystallinity of Gels

The primary concern was to prepare gels without any crystallinity and to examine the crystallinity, if any, developed after thermal treatments.

### Gel Preparation Procedures

Gel preparation procedures based on two different approaches have been developed. The first approach consists of the reactions of all or most of the reactants in nonaqueous solvents. Initially, all or most of the reactants were allowed to mix and react with each other in the presence of a catalyst. Subsequently, the gelation was initiated by one of the following ways: (a) adding a limited amount of water, and (b) by exposing the final solution to atmospheric moisture.

The second approach is based on the initial partial hydrolysis of tetraethyl orthosilicate by the addition of a limited amount of water and an acid catalyst before the addition of other constituents. Subsequently, aqueous solutions of the other constituents were added for the reaction and gelation.

The gel preparation procedures developed for the compositions selected for the present investigations are described separately for each composition in a later section of this report.

### Thermal Treatment of Gels

The main objective of the thermal treatment is to remove the volatile organic or inorganic compounds or groups (such as alcohols, nitrates, hydroxyl groups and alkoxy groups) by volatilization and decomposition, and thus to transform the gel to homogeneous non-crystalline oxides. After the preparation, the gel may be visualized as a system of solid character in which the macromolecules are dispersed in a solvent and somehow constitute a coherent structure. Thus, it contains the solvent, the alcohols produced by the reaction, chemically bonded unreacted residual alkoxy groups, and residual unreacted water. Hence, the following phenomena might occur during the thermal treatment.

- Removal of solvents and the release of free alcohols at a lower temperature.
- Hydrolysis of the chemically bonded alkoxy groups with the atmospheric moisture or with the excess water incorporated during the preparation of gel.
- Oxidation and removal of organic molecules as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at a later stage of thermal treatment. The presence of oxygen is beneficial at this stage.
- Formation of micropores with highly reactive surfaces after the removal of solvents and residual organic groups.
- Collapsing the pores to form a dense structure or to form closed pores.

The main concern for the thermal treatment in the present work is to develop a procedure which would secure the maintenance of gel purity. Hence, a time-consuming thermal treatment procedure is not desirable. To realize this objective various combinations of steps involving humidity treatment, heating in steps and different rates of heating were used. The thermal treatment procedures followed for removal of organics from the gels of the compositions selected for the present investigation are described separately for each composition.

#### Characterization of Gels

The physico-chemical nature of gels is controlled by the method of preparation. Hence, attempts were made to characterize gels prepared by different procedures to know the physico-chemical properties of the gels after thermal treatments. The following aspects were examined.

- Color.
- Carbon content.
- Crystallinity.
- Specific surface areas.

### Conversion of Gels to Glasses by Melting

The melting of gels were done to achieve the following:

- Time and temperature required to obtain glasses free from melting defects.
- Reduction of hydroxyl content of the glass.
- Gels of one composition but prepared by different procedures were melted in order to determine the Rayleigh Scattering loss in relation to the method of preparation and the heat treatment of the glasses. Also, one glass sample was prepared by conventional techniques using the same composition for comparison.
- Gels of one composition but prepared by different procedures were melted to investigate the phase separation behavior of gel-derived glasses.

### Characterization of Glasses

The glasses obtained from gels prepared by different procedures were characterized with respect to the following aspects:

- Melting defects (i.e., bubbles and particles)
- Microstructures evaluated by Electron Microscopy and Small Angle X-ray Scattering
- Homogeneity evaluated by Light Scattering (Rayleigh Scattering)
- Molecular Structures evaluated by
  - a. Infrared Spectroscopy
  - b. Raman Spectroscopy.

The Raman spectroscopic measurements were performed at the Materials Research Laboratory of the Pennsylvania State University. Small angle x-ray scattering was carried out at the Jet Propulsion Laboratory, Pasadena, California. Rayleigh Scattering studies were performed at the Vitreous State Laboratory of Catholic University of America, Washington, D.C.

## PART IB. EXPERIMENTAL WORK ON AND RESULTS OF COMPOSITION 1

The experimental results of the present work have been divided into the following activities:

- Choice of composition.
- Gel preparation procedures.
- Thermal treatment of gels.
- Characterization of gels.
- Conversion of gels to glasses by melting.
- Characterization of glasses.

### Choice of Composition

The objective of the initial work was to develop the gel preparation procedures and to characterize glasses obtained from those gels. A composition containing a high proportion of alkali oxide and being outside the metastable liquid-liquid immiscibility zone was selected for the present study. The composition was as follows (in weight percent)  
 $\text{SiO}_2$ :60;  $\text{B}_2\text{O}_3$ : 15;  $\text{Na}_2\text{O}$ :25.

### Gel Preparation Procedures

Several preparation procedures were developed during the initial period (Final Progress Report, JPL Contract 955361)<sup>(3)</sup> of this program. Three preparation procedures using three different sources of  $\text{Na}_2\text{O}$  were selected from the procedures developed earlier. However, some modifications of the procedures were made during the present work. The preparation procedures are described below.

Procedure 1-1. Starting Compounds: Tetraethyl Orthosilicate  
Boric Acid  
Sodium Methyrate

Tetraethyl orthosilicate was mixed with about 1/2 its volume of anhydrous ethanol. The solution was heated to 40 C, and after 10 minutes tetraethyl orthosilicate was partially hydrolysed with a small proportion of acidified water [2 mol  $\text{H}_2\text{O}$ /mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ]. The pH of the solution was five after the addition of acidified water. A small volume of acetylacetone (3 ml/100 ml of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) was added after the addition of acidified water. After stirring the solution for 1/2 hour, boric acid dissolved in boiling methanol (30 g/100 ml) was added to the solution. The pH of the solution was about six. After 1 hour, sodium methylate dissolved in methanol was added to the mixture. The pH increased to about 10. The solution was stirred for 45 minutes. After 45 minutes, a mixture of water and ethanol (1:4 ratio) was added to the solution to introduce more water for further hydrolysis and gelation. The amount of water added was 5.8 mols per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The solution gelled within 5 minutes on addition of the alcohol water mixtures.

Procedure 1-II. Starting Compounds: Tetraethyl Orthosilicate

Boric Acid

Sodium Nitrate

Tetraethyl orthosilicate was mixed with about 1/2 its volume of anhydrous ethanol. The solution was heated to approximately 40 C. After 5 minutes, a requisite amount of water acidified with dilute HCl was added for the partial hydrolysis of tetraethyl orthosilicate. After stirring for 1/2 hour, boric acid dissolved in methanol (30 g/100 ml) was added to the solution. The solution was stirred for about 1 hour. Finally, a dilute aqueous solution of sodium nitrate was added to the mixture. The total amount of water added with the sodium nitrate was several times the amount of water required for the complete hydrolysis of tetraethyl orthosilicate. The proportion of water was 20 mols per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ .

Procedure 1-III. Starting Compounds: Tetraethyl Orthosilicate

Trimethyl Borate

Sodium Acetate

Tetraethyl orthosilicate was mixed with 1/2 its volume of anhydrous ethanol. The mixture was heated to 40 C, and was hydrolysed in excess water in the presence of an acid catalyst with a pH of approximately

2. The amount of water added was about 11 mols per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . After stirring for 1/2 hour, trimethyl borate was added and the mixture was stirred for 45 minutes. Finally, a sodium acetate solution was added rapidly to the solution with continuous stirring. The gelation took place after 1/2 hour.

#### Thermal Treatment of Gels

The thermal treatment of gels was carried out to achieve the following two objectives:

- The removal of organics.
- The removal of hydroxyl groups.

#### Treatment for the Removal of Organics From Gels

The thermal treatment procedure used for the removal of organics consisted of heating in steps and a slow rate of heating.

The thermal treatment procedure consisted of the following steps:

- (1) Drying in air under an infrared lamp ( $\sim 60^\circ\text{C}$ ) for 2 to 3 days.
- (2) Drying in an air oven at approximately  $150^\circ\text{C}$  for 48 to 60 hours.
- (3) Heating from  $150^\circ\text{C}$  to  $600^\circ\text{C}$  at the rate of  $10^\circ\text{C}/\text{hour}$ .
- (4) Holding at  $600^\circ\text{C}$  for about 20 hours.

It was observed that the spraying of water during the initial thermal treatment under the infrared lamp was beneficial for the removal of organic groups during the firing cycle. Initial thermal treatments of "as prepared" gels in a humidity chamber were also beneficial for the removal of organic groups.

Treatment for the Removal of Hydroxyl  
Groups From the Gels

The following steps were taken for the removal of hydroxyl groups:

- (1) Baking in an oven.
- (2) Passing dry  $O_2$  through the porous gels at elevated temperatures.
- (3) Passing thionyl chloride ( $SOCl_2$ ) vapor carried by dry oxygen through the porous gels at elevated temperatures.
- (4) Passing carbon tetrachloride ( $CCl_4$ ) vapors carried by dry oxygen through porous gels at elevated temperatures.
- (5) Subsequent melting of the thionyl chloride treated gels.
- (6) Melting of dehydrated gels in a nitrogen atmosphere.

Experimentation involving dehydration procedures were designed to remove as much water (hydroxyl groups) as possible at low temperatures before melting. Initial experimentation involving Composition I gel powders utilized a horizontal tube furnace while passing either dry oxygen only (dewpoint:  $-60^\circ C$ ), or dry oxygen bubbled through liquid thionyl chloride vapors, for varying time periods. These procedures reduced the  $OH^-$  content in the subsequently melted glasses, but thionyl chloride treatment caused an extensive liquid-liquid immiscibility in the melts.

Subsequently, the procedures were modified and a closed vertical flow apparatus was used for dehydration. A diagram of this system is shown in Figure 2. The vertical flow column was packed with gel powder while dry oxygen or dry oxygen-carrying thionyl chloride or carbon tetrachloride vapors was forced upward through the packed column. This allowed for a more intimate contact between the gel powder and the dry gases. The temperature within the furnace was raised at a rate of  $50^\circ C$ /hour to optimal dehydration temperatures ( $300^\circ C$  for Procedure III



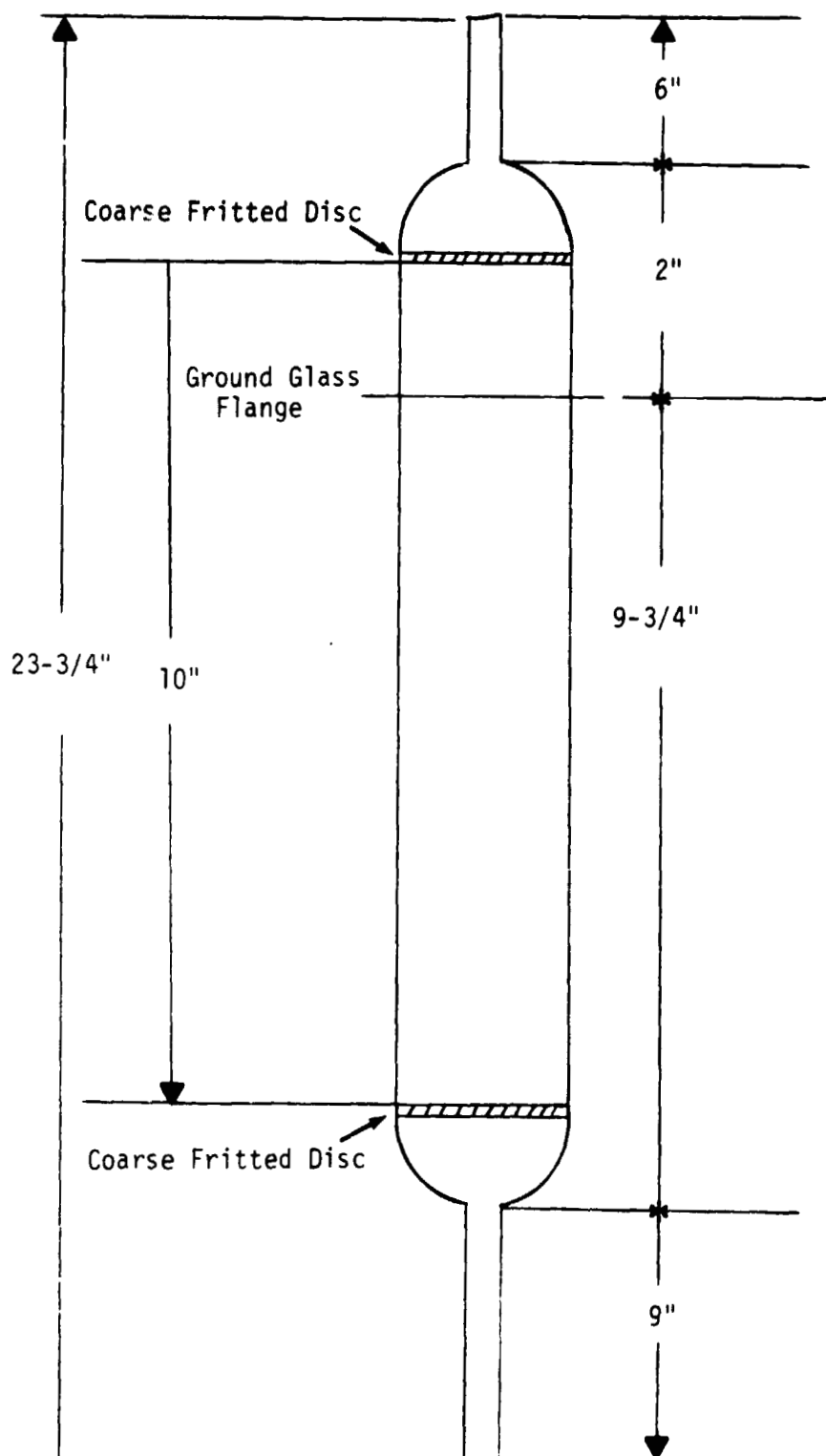


FIGURE 2. VERTICAL FLOW DEHYDRATION APPARATUS

powders, 200 C for Procedure I and III powders). Powders that were kept at these temperatures, with the longest period of dry oxygen flow, produced glasses of the lowest OH content. As in the earlier experimentation, gel powders treated with thionyl chloride vapor showed a definite liquid-liquid immiscibility in the melts. The thionyl chloride treatment was therefore discontinued. The gel powders treated with only dry oxygen or dry oxygen carrying carbon tetrachloride vapors produced clear melts of reduced OH content. Results of dehydration experimentation and hydroxyl determination are recorded in Table 11 appearing later in the report.

### Characterization of Gels

#### Color of Gels

The results of thermal treatments at various temperatures and times and their effect on color are summarized in Table 2. It is evident from the results that the removal of organics from gels is related to the gel preparation procedure as well as to the thermal treatment procedures.

#### Carbon Content

The total carbon content of gels prepared by different procedures and heat treatment at 600 C for 40 hours was analyzed. The results are given below:

<u>Gel Preparation Procedure</u>	<u>Total Carbon Content (wt %)</u>
1- I	0.1
1- II	0.1
1- III	0.6

TABLE 2. COLOR OF GELS AFTER HEAT TREATMENT

Gel Preparation Procedure	Heat Treatment	Appearance
1-I	150 C for 48 hours	Tan
1-I	150 C for 48 hours and 600 C for 5 hours	Grey
1-I	150 C for 48 hours 600 C for 40 hours	Grey
1-II	150 C for 48 hours	White
	150 C for 48 hours and 600 C for 5 hours	White
	150 C for 48 hours 600 C for 40 hours	White
1-III	150 C for 48 hours 600 C for 40 hours	Black
	150 C for 48 hours 600 C for 5 hours	Black with grey particles
	150 C for 48 hours 600 C for 40 hours	"

### Crystallinity

Gel samples after thermal treatments at 600 C for different time periods were examined by x-ray powder pattern techniques. The results are given in Table 3.

### Surface Areas

The surface areas of gels prepared by different procedures were measured on a micrometric instrument over a range of temperatures to get an idea about the change of surface area with temperature.

Two sets of experiments were performed to study the change of surface area as a function of temperature. In the first series of experiments, the surface areas were measured on a micrometric instrument over a range of temperatures in situ. The gels were held at each rising temperature for 1/2 hour before the measurement of surface area. The heating was done while the samples were under the micrometric instrument. In this series of experiments, the fresh gel sample was heat treated inside the micrometric instrument and was evacuated after the heat treatment, and, subsequently, the surface area was measured. Consequently, the surface was not exposed to the atmosphere after the heat treatment and surface pores were cleaned under vacuum after the volatilization of the solvents. Moreover, the time was short, so the time may not have been long enough for reaching the equilibrium surface area at that temperature, because at higher temperatures the formation of pores as well as the closing of pores might occur simultaneously. Results of the first set of experiments are shown in Table 4.

In the second series of experiments, the gels were heat treated at different temperatures for different time periods in a furnace under air atmosphere. The samples were then taken out, and stored in atmospheric conditions. Subsequently, the surface area of the heat treated gels were measured. Moreover, the period of heat treatment was longer than that of the first set of experiments. Consequently, the heat treatment at higher temperatures for longer time periods might have caused opening as well as closing of the pores. Results of these experiments are shown in Table 5.

TABLE 3. CRYSTALLINITY OF GELS AFTER VARIOUS THERMAL TREATMENTS

Gel Preparation Procedure	Thermal Treatment	Crystallinity
1-I	13 Hours at 500 C	Noncrystalline
1-I	24 Hours at 500 C	Noncrystalline
1-I	2 Hours at 600 C	Noncrystalline
1-I	40 Hours at 600 C	Noncrystalline
1-II	After Air Dryup	Crystalline, (Due to $\text{NaNO}_3$ )
1-II	2 Hours at 500 C	Crystalline
1-II	2 Hours at 600 C	Crystalline
1-II	40 Hours at 600 C	Crystalline
1-III	13 Hours at 500 C	Noncrystalline
1-III	24 Hours at 500 C	Noncrystalline
1-III	2 Hours at 600 C	Noncrystalline
1-III	40 Hours at 600 C	Noncrystalline

TABLE 4. SURFACE AREAS OF GELS PREPARED BY DIFFERENT PROCEDURES  
AFTER ONE-HALF HOUR HEAT TREATMENT AT DIFFERENT TEMPERATURES

Gel Preparation Procedure	Temperature of Treatment	Surface Area m <sup>2</sup> /g
1-I	150 C	40.00
1-I	300 C	42.00
1-I	500 C	<u>0.00</u>
1-II	150 C	6.00
1-II	300 C	6.00
1-II	400 C	6.00
1-II	500 C	<u>0.00</u>
1-III	150 C	2.00
1-III	300 C	25.00
1-III	400 C	100.00
1-III	500 C	11.00

TABLE 5. SURFACE AREAS OF GEL SAMPLES AFTER DIFFERENT THERMAL TREATMENTS

Gel Preparation Procedure	Heat Treatment Temperature (C)	Period of Heat Treatment (Hours)	Surface Area (m <sup>2</sup> /g)
1-I	200	2	15
1-I	200	4	22
1-I	250	2	15
1-I	250	4	13
1-I	250	6	15
1-I	300	2	14
1-I	300	4	15
1-I	300	6	6
1-II	200	2	30
1-II	200	4	33
1-II	275	2	33
1-II	275	4	34
1-II	275	6	21
1-II	350	2	20
1-II	350	4	1
1-II	350	6	0.37
1-III	200	2	40
1-III	200	6	51
1-III	300	2	38
1-III	300	4	46
1-III	400	2	49
1-III	400	4	50
1-III	400	6	42

### Conversion of Gels to Glasses by Melting

Gel powders were melted to address the following objectives.

- To study the molecular structure of gel-derived glasses.
- To study the effect of process parameters of melting on the removal of hydroxyl groups.

#### Melting of Gel Powders for Studying the Molecular Structure of Gel-Derived Glasses

The gels prepared by different procedures were heat treated up to 500 C to remove organic matters and were subsequently melted at 1000 C to obtain clear glass by eliminating residual carbons. The results are summarized in Tables 6, 7, and 8.

#### Melting of Gel Powders for Studying the Removal of Hydroxyl Groups

Initially, Composition 1 gel powders having no dehydration treatments were melted. These melts were used for comparison after determination of OH content in the dehydrated melts. For this, gel powders were placed in a platinum crucible and left for approximately 16 hours at 500 C. The temperature was then raised quickly to 1200 C and held for 5 hours. After melting, clear glass patties were made by pouring the melt onto a hot stainless steel plate and annealing for 1 hour at 580 C.

Dehydrated gel powders were treated at optimal dehydration temperatures, then the temperature was raised to 500 C with continued dry oxygen flow. These powders were kept at 500 C for approximately 16 hours, then raised to melting temperatures quickly (with no dry oxygen flow). Pouring and annealing procedures of these melts were the same as for the others. Gel powders having thionyl chloride treatment showed a liquid-liquid immiscibility in the melts. Gel powders having only dry



TABLE 6. EFFECT OF TIME AND TEMPERATURE ON THE REMOVAL OF RESIDUAL CARBON DURING THE MELTING OF GELS PREPARED BY PROCEDURE 1-1

Experiment No.	Thermal Treatment Prior to Melting	Melting Temperature (C)	Melting Time (Hours)	Appearance
(1)	After Infrared Drying	1000	2	Grey Colors, Transparent Numerous Bubbles
(2)	After Infrared Drying	1000	3	Colorless and Transparent, Less Number Bubbles
(3)	After Infrared Drying	1000	4	Colorless and Transparent, much Less Bubbles
(4)	After Infrared Drying	1000	5	Highly Transparent, Bubble Undetected
(5)	After Infrared Drying	1100	2	Quite Transparent and Colorless, no Detectable Bubbles
(6)	After Infrared Drying	1100	3	Highly Transparent Colorless, no Bubbles
(7)	After Infrared Drying	1200	1	Transparent Colorless, no Bubbles
(8)	After Infrared Drying	1200	2	Transparent Colorless, no Bubbles
(9)	After Thermal Treatment up to 500 C	1000	5	Transparent Glass after 5 Hours
(10)	After Thermal Treatment up to 500 C	1100	3	Transparent Glass
(11)	After Thermal Treatment up to 500 C	1200	2	Transparent Glass

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TABLE 7. EFFECT OF TIME AND TEMPERATURES ON THE REMOVAL OF RESIDUAL CARBON DURING THE MELTING OF GELS PREPARED BY PROCEDURE 1-II

Experiment No.	Thermal Treatment Prior to Melting	Melting Temperature (C)	Melting Time (Hours)	Appearance
(1)	Thermal Treatment up to 500 C	1000	1	Transparent
(2)	Thermal Treatment up to 500 C	1000	2	Transparent
(3)	Thermal Treatment up to 500 C	1000	4	Transparent

TABLE 8. EFFECT OF TIME AND TEMPERATURE ON THE REMOVAL OF RESIDUAL CARBON DURING THE MELTING OF GELS PREPARED BY PROCEDURE 1-III

Experiment No.	Thermal Treatment Prior to Melting	Melting Temperature (C)	Melting Time (Hours)	Appearance
(1)	Thermal Treatment up to 500 C	1000	1	Transparent with some Black Residue
(2)	Thermal Treatment up to 500 C	1000	2	Transparent with some Black Residue
(3)	Thermal Treatment up to 500 C	1000	4	Transparent
(4)	Thermal Treatment up to 500 C	1200	1	Transparent with some Residue
(5)	Thermal Treatment up to 500 C	1200	2	More Transparent
(6)	Thermal Treatment up to 500 C	1200	4	Transparent

oxygen or dry oxygen-carrying carbon tetrachloride vapor during dehydration produced clear melts with reduced OH content.

Further attempts at the removal of hydroxyl groups of Composition 1 gel glasses were made during the melting process. During the melting process, a platinum crucible containing glass made from dehydrated gel powders was placed in a furnace. The platinum crucible was covered with an inverted high purity alumina crucible to isolate the gel glass from atmospheric water and oxygen. Two tubes extended through the top of the furnace, through the "bottom" of the inverted alumina crucible into the isolated area. These tubes consisted of:

- (1) A platinum tube reaching into the contents of the platinum crucible, for bubbling dry nitrogen (dewpoint  $\sim -59$  C) through the glass during melting.
- (2) An alumina tube reaching only inside the isolated area for the passage of dry nitrogen to produce a dry nitrogen atmosphere over the melt.

In addition, a thermocouple was placed in this isolated area to monitor the temperature near the melt. Before these melting procedures took place, the entire furnace set-up was heated to approximately 500 C to remove surface absorbed water from the materials of the set-up just described. The melting procedure was as follows: the furnace was at room temperature during loading, for safety purposes. The temperature of the furnace was raised to 500 C in 1 hour. At this time, both flows of dry nitrogen were started: i.e., flow through the contents of the platinum crucible, and dry nitrogen flow above the melt. The temperature was raised to 1300 C in approximately 3 hours. The dry nitrogen flows continued at 1300 C for 4 hours. Finally, the tubes were removed and glass patties were poured and annealed for 1 hour at 580 C. Transparent bubble-free glasses were obtained by this procedure. The hydroxyl content of these glasses were far superior to the OH content of the earlier gel glasses.

### Characterization of Glasses

The molecular structure of glasses obtained from gels prepared by different methods were investigated by Infrared Spectroscopy and Raman Spectroscopy.

#### Infrared Spectroscopic Studies

The infrared spectra of the glasses were taken by the KBr pellet technique; the results showing the change in the position of the absorption band due to Si-O-Si stretching ( $\nu$   $\text{cm}^{-1}$ ) are given in Table 9.

#### Raman Spectroscopic Studies

The Raman spectra of glass samples in the fiber form were measured in the 200-to-1300  $\text{cm}^{-1}$  region. This region contains the characteristic vibrations of the glass structure. The Raman spectroscopic measurement was done at the Materials Research Laboratory of the Pennsylvania State University. The work was done by T. Furukawa under the supervision of Professor W. B. White. The melting history of glasses sent for the Raman spectroscopy are given in Table 10.

The instrument used for the Raman spectroscopic studies was an Spex Model 1401. The excitation source was a 514.5 nm green line, 400-700 MW.

The results of the Raman spectroscopic studies can be summarized as follows:

- (1) All the glasses produce similar Raman spectra.
  - A weak band at 1475  $\text{cm}^{-1}$ ; B-O stretching.
  - A strong band at 1090  $\text{cm}^{-1}$ ; Si-O (nonbridging) stretching.
  - A fairly sharp peak at 630  $\text{cm}^{-1}$ ; may be due to some boroxy group or borosilicate group.
- (2) Samples 4 and 6 seem to have a slightly stronger 1090  $\text{cm}^{-1}$  band compared to the others, which indicates more Si-O nonbridging bonds.

TABLE 9. CHARACTERISTICS OF THE IR ABSORPTION BANDS DUE TO Si-O-Si STRETCHING OF DIFFERENT GLASSES

Gel Preparation Procedure	Melting Temperature (C)	Melting Time (Hours)	Position of Absorption Band due to Si-O-Si Stretching ( $\nu$ cm <sup>-1</sup> )
1-I	1000	2	1000
1-I	1000	3	1000
1-I	1000	3	1000
1-I	1100	2	1000
1-I	1200	1	1000
1-I	1200	2	1000
1-I	1200	4	1020
1-I	1400	2	1080
1-III	1200	1	1020
1-III	1200	2	1040
1-III	1200	4	1040

TABLE 10. MELTING HISTORIES OF THE SAMPLES FOR  
THE RAMAN SPECTROSCOPIC STUDIES

Sample No.	Gel Preparation Procedures	Melting Temperature (C)	Melting Time (Hours)
1	1-I	1200	2
2	1-I	1200	4
3	1-II	1000	2
4	1-II	1000	6
5	1-II	1200	1
6	1-II	1200	3-1/2
7	Conventional Glass Batch	1000	2
8	Conventional Glass Batch	1200	6

- (3) No bands due to  $H_2O$  or OH were detected.
- (4) All the mixtures luminesce in the red region.

#### Determination of Hydroxyl Content

Composition 1 glass samples were used for determining the hydroxyl content. The glass samples were ground and polished to a thickness of 2 to 4 mm for taking infrared spectra. The influence of water as a polishing fluid was compared to the glass samples polished with kerosene. Infrared spectra was taken at room temperature and at 200 C to determine the effect of heating the sample. It was observed that heating the sample to 200 C showed no difference in the intensity of the spectra.

The Lambert-Beer Equation was used to calculate the hydroxyl content of the glasses. Absorbance values were determined from the infrared spectra using the baseline method. The extinction coefficient was taken from the work of Pearson et al <sup>(4)</sup>, who determined the extinction coefficient due to hydroxyl groups at 2.73  $\mu m$  in the alkali-borosilicate glass of the composition:  $SiO_2:45$ ;  $B_2O_3:35$ ;  $Na_2O:20$  (mole percent). This extinction coefficient is the only one available for our use in hydroxyl determination. Taking into account the density of Composition 1 glass ( $2.27 \text{ g/cm}^3$ ), the hydroxyl contents in ppm were calculated. These results are reported in Table 11.

#### Phase Separation With Thionyl Chloride Treatment

The melting of thionyl chloride vapor treated gels resulted in the separation into two liquids - a highly fluid top layer and a highly viscous bottom layer. The top layer became completely white and opaque upon cooling, the bottom layer remained transparent. The distribution of silicon, sodium, sulfur, and chlorine in the two layers were determined by the EDAX technique. The results showed that the top layer had a high proportion of sodium and sulfur and traces of chlorine. The bottom layer had mostly silicon and a small amount of chlorine. It is evident that sodium ions and sulfur, present as sulfate ions, partitioned into the top layer which was practically devoid of silica. Whereas, the



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TABLE 11. HYDROXYL CONTENT IN COMPOSITION 1 GLASSES (ALL THE SAMPLES WERE DRIED IN OVEN AT 150 C FOR 48 HOURS BEFORE DEHYDRATION TREATMENTS)

Gel Preparation Procedure	Dehydration Treatment			Melting of Dehydrated Gel Powders			OH <sup>-</sup> Concentration		Sample Temperature During IR Measurement (C)
	Dehydrating Agent Used	Dehydration Temperature (C)	Dehydration Time (Hour)	Temperature (C)	Time (Hour)	Atmosphere	Moles/Liter	PPM d=2.27g/ml	
1-I	-	500	48	1300	4	Air	.04	299.5	20
1-I	-	500	48	1300	4	Air	.04	299.5	200
1-I	Dry O <sub>2</sub>	200 and 500	1 ~12	1200	5	Air	.027	202.5	20
1-II	Dry O <sub>2</sub>	200 and 500	1 ~12	1300	4	N <sub>2</sub> (Bubbled)	.00165	12.3	20
1-II	-	500	48	1200	4	Air	.068	505.2	20
1-II	-	500	48	1200	4	Air	.068	509.2	200
1-II	O <sub>2</sub>	300	5	1200	4	Air	.0254	190.3	20
1-II	C <sub>2</sub>	300	5	1200	4	Air	.0259	194.2	200
1-II	Dry O <sub>2</sub> , SOCl <sub>2</sub> Vapor	300	1	1200	4	Air	.0203	152.4	20
1-II	Dry O <sub>2</sub>	300 and 500	1 ~12	1200	5	Air	.0175	130.8	20
1-II	Dry O <sub>2</sub>	300 and 500	1 ~12	1200	5	Air	.0175	130.8	20
1-II	Dry O <sub>2</sub> , CCl <sub>4</sub> Vapor	300 and 500	6 ~18	1200	5	Air	.0156	116.7	20
1-III	Dry O <sub>2</sub>	300 and 500	1 ~12	1200	5	N <sub>2</sub> (Bubbled)	.000786	5.9	20
1-III	-	500	48	1300	5	Air	.0418	313.2	20
1-III	-	500	48	1300	5	Air	.0418	313.2	200
1-III	O <sub>2</sub>	300	5	1300	5	Air	.0376	281.4	20
1-III	Dry O <sub>2</sub>	200 and 500	1 ~12	1200	5	Air	.0188	140.7	20
Conventional Glass	-	500	48	1300	5	Air	.0297	222.2	20
*Conventional Glass	Dry O <sub>2</sub>	300 and 500	1 ~12	1300	5	N <sub>2</sub>	.000399	2.98	20

\*During melting of these batches, dry nitrogen gas was bubbled through the melts.

bottom layer was devoid of sodium ions and had silica as its major constituent. The determination of the distribution of boron was not possible with this technique because of its low atomic weight.

A large liquid-liquid immiscibility gap<sup>(5)</sup> exists in the system  $\text{SiO}_2\text{-Na}_2\text{O-Na}_2\text{SO}_4$  at 1200 C. Presumably, thionyl chloride during the dehydration treatment reacts with the sodium ions and residual water to form sodium sulfate which causes the liquid-liquid separation during melting. The presence of a large proportion of sulfur and sodium in the top fluid layer substantiate the explanation suggested.

PART II. GEL-DERIVED GLASSES FOR RAYLEIGH SCATTERING  
STUDIES (EXPERIMENTAL RESULTS)

The experimental results of the present work on Rayleigh Scattering studies have been divided into the following activities.

- Choice of composition.
- Choice of starting compounds.
- Preparation of gels.
- Thermal treatment of gels.
- Characterization of gels.
- Melting of gels and conversion to glasses.
- Preparation of glass by conventional method (for comparison).
- Preparation of glass samples for Rayleigh Scattering.
- Rayleigh Scattering studies.

Choice of Composition

The following composition was selected for the Rayleigh Scattering studies:  $\text{SiO}_2$ :55;  $\text{B}_2\text{O}_3$ :25;  $\text{Na}_2\text{O}$ :20 (weight percent). This composition, designated as Composition 2, was selected because some previous work<sup>(2)</sup> on Rayleigh Scattering had been done with this composition prepared by the conventional technique. Thus, we were in a position to compare the results of the gel-derived glasses with those of conventional glasses.

Starting Compounds

The following starting compounds were used as sources of different oxides in the different procedures. Reagent grade chemicals were used for the present investigation.

<u>Oxide</u>	<u>Source</u>
$\text{SiO}_2$	Tetraethyl Orthosilicate
$\text{B}_2\text{O}_3$	Boric Acid
	Trimethyl Borate
$\text{Na}_2\text{O}$	Sodium Methylate
	Sodium Nitrate
	Sodium Acetate

### Gel Preparation Procedures

Gel preparations by three procedures using three different sources of  $\text{Na}_2\text{O}$  were based on the procedures developed earlier. However, some modifications of the procedures were made to achieve more homogeneity in the gels and also to remove a maximum amount of organics during initial heat treatment ( $\leq 500^\circ\text{C}$ ). The preparation procedures are described below.

Procedure 2-I. Starting Compounds: Tetraethyl Orthosilicate  
Boric Acid  
Sodium Methylate

Tetraethyl orthosilicate was mixed with three times its volume of anhydrous ethanol. The solution was stirred for approximately 5 minutes and then a small amount of 1N. HCL [0.0002 mole HCL/mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ] was added followed by the addition of acetyl acetone [5 ml/100 ml  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ]. The solution was partially hydrolyzed for a period of about 1 hour by stirring the solution continuously. The pH of the solution was 3.6. The solution was cooled to room temperature, boric acid dissolved in boiling methanol (30 g/100 ml) was added, and stirring was continued for about 2 hours. The pH of the solution was 3.6. To this mixture sodium methylate and/as anhydrous methanol (1:1 by volume) was added. The pH increased to about 10. The solution was stirred for about 45 minutes and then a requisite amount of anhydrous ethanol was added to obtain a concentration of approximately 40 grams silica per liter of the solution. After the addition of anhydrous ethanol the solution was stirred for a further period of about 1/2 hour. The solution gelled in 3 hours.

Procedure 2-II. Starting Compounds: Tetraethyl Orthosilicate  
Boric Acid  
Sodium Nitrate

Tetraethyl orthosilicate was mixed with three times its volume of anhydrous ethanol. The solution was stirred for approximately 5 minutes and then approximately 0.5 mol water [per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ] acidified with HCl [0.0004 mole HCl/mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ] was added for partial hydrolysis of tetraethyl orthosilicate. The solution was heated to approximately 40 C and stirring was continued for about 1 hour. The pH of the solution was 2.8. Boric acid dissolved in anhydrous methanol (approximately 30 g/100 ml) was added to the partially hydrolyzed tetraethyl orthosilicate, and stirring was continued for 1 hour. The pH of the solution was 2.4. Finally, a dilute aqueous solution of sodium nitrate (approximately 17 g/100 ml) was added to the mixture and stirring was continued for 3 hours. The concentration of the solution was approximately 70 grams silica per liter. The pH was 3.2. The solution was slowly evaporated at approximately 40 C to gel in 3 days.

Procedure 2-III. Starting Compounds: Tetraethyl Orthosilicate  
Trimethyl Borate  
Sodium Acetate

Tetraethyl orthosilicate was mixed with three times its volume of anhydrous ethanol. The solution was stirred for about 5 minutes and then one molar ratio of water acidified with concentrated HCl [0.02 mol HCl/mole  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ] was added for partial hydrolysis of tetraethyl orthosilicate. The solution was heated to approximately 40 C and stirred for about 1 hour. The pH was 0.2. The solution was cooled to room temperature and a requisite amount of trimethyl borate was added and the mixture was stirred for another 3 hours. The pH was 0.4. Finally, a buffer solution of 0.5M sodium acetate (prepared by dissolving crystalline sodium acetate in water to which acetic anhydride had been added) was added and the solution was stirred for 2 to 3 minutes. The concentration of the solution was approximately 45 grams silica per liter and the pH was 5.5. The solution gelled in about 1 hour.

### Thermal Treatment of Gels

The behavior of Composition 1 gels towards thermal treatment indicate that the removal of organics from the gels is related to the gel preparation procedure as well as to the thermal treatment procedures. Because the glass composition chosen for Rayleigh Scattering studies was different and some modifications were made in the gel preparation procedures, it was considered necessary to examine the behavior of gels so produced towards thermal treatment. Besides, some modifications were made in thermal treatment procedures to achieve the maximum removal of organics. The thermal treatment procedures used for the removal of organics consisted of humidity treatment, heating in steps and a slow rate of heating. The thermal treatment procedures consisted of different combinations of the following steps:

- (1) Humidity treatment at 70 C and RH 95 percent for 12 hours and 24 hours.
- (2) Drying in air under infrared lamp (approximately 60 C) for 2 to 3 days.
- (3) Drying in a microwave oven.
- (4) Heating up to 500 C at the rate of 100 C/hour and holding at 500 C for 12 hours; making a total heat treatment of 17 hours.
- (5) Heating up to 500 C in steps and holding at 500 C for 4 hours, making a total heat treatment of 48 hours.
- (6) Heating up to 500 C in steps and holding at 500 C for 8 hours (making a total heat treatment of 96 hours) in the presence of  $O_2$ .
- (7) Heating up to 500 C in steps with occasional moistening of the samples with water from time to time. This heating schedule covered a total period of approximately 200 hours.

The results of thermal treatment are summarized in Tables 12, 13, and 14. It was observed that:

- (a) The use of microwave oven drying as a step in the heat treatment procedure was not helpful for the removal of organics.
- (b) Humidity treatment was beneficial for removing organics from the gel prepared by Procedure 2-I. However, the same effect was not apparently evident in Gels prepared by Procedure 2-III.
- (c) Heat treatment for longer periods in the presence of oxygen was beneficial, but not very effective for complete removal of organics.
- (d) Occasional spraying of the samples with water was found to be more beneficial for removing organics from the gel. However, complete removal of organics was not achieved with this procedure.

#### Characterization of Gels

Gel powders were characterized after the thermal treatments. The following aspects of the physico-chemical nature of the gels were examined.

#### Color of Gels

The results of thermal treatments at various temperatures and times are summarized in Tables 12, 13, and 14. It is evident from the results that the removal of organics from the gels is related to the gel preparation procedure as well as the thermal treatment procedures.

TABLE 12. RESULTS OF THERMAL TREATMENT OF GELS FOR REMOVAL OF ORGANICS

Gel Preparation Procedure	Heat Treatment	Appearance
2-I	Humidity treatment/12 hours, IR dry/2 days, Heated to 500 C/48 hours heating schedule	Whitish grey, some black particles
2-I	Humidity treatment/24 hours, IR dry/2 days, Heated to 500 C/48 hours heating schedule	Mixture of white, whitish grey and greyish black particles
2-I	IR dry/2 days, Heated to 500 C/48 hours heating schedule	Mixture of grey and black particles
2-III	IR dry/2 days, Humidity treatment/12 hours, Microwave oven drying, Heated to 500 C/17 hours heating schedule	Black
2-III	IR dry/2 days, Humidity treatment/12 hours, Microwave oven drying, Heated to 500 C/48 hours heating schedule	Black
2-III	Humidity treatment/12 hours, Microwave oven drying, Heated to 500 C/17 hours heating schedule	Black



TABLE 13. INITIAL HEAT TREATMENT OF COMPOSITION 2  
GELS IN PRESENCE OF OXYGEN

Gel Preparation Procedure	Heat Treatment Schedule	Appearance
2-I	Humidity treatments/12 hrs IR dry/2 days. Heated to 500 C/96 hrs heating schedule.	Mixture of white, whitish grey and black particles.
2-I	Humidity treatment/24 hrs IR dry/2 days. Heated to 500 C/96 hrs heating schedule.	Mixture of white, greyish white and some black particles.
2-I	Humidity treatment/24 hrs Heated to 500 C/96 hrs heating schedule.	Mixture of white, whitish grey and some black particles.
2-III	Humidity treatment/12 hrs IR dry/2 days. Heated to 500 C/96 hrs heating schedule.	Mixture of grey and black particles.
2-III	IR dry/2 days. Heated to 500 C/96 hrs heating schedule.	Mixture of grey and black particles.

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TABLE 14. INITIAL HEAT TREATMENT OF COMPOSITION 2 GELS  
WITH OCCASIONAL MOISTENING WITH WATER

Gel Preparation Procedure	Heating Schedule	Appearance
2-I	Humidity treatment/24 hrs IR dry/2 days. Heating upto 500 C/ ~200 hrs heating schedule.	Dirty white particles.
2-I	Humidity treatment/12 hrs IR dry/2 days. Heating upto 500 C/ ~200 hrs heating schedule.	Dirty white particles.
2-III	IR dry/2 days. Heating upto 500 C/ ~200 hrs heating schedule.	Mixture of dirty white, grey, and a few black particles.
2-III	Humidity treatment/12 hrs IR dry/2 days. Heating upto 500 C/ ~200 hrs heating schedule.	A mixture of dirty white, grey, and a few black particles.

### Thermogravimetric Analysis

Thermogravimetric analyses were done on IR dried samples prepared by Procedures 2-I, 2-II, and 2-III under air atmosphere up to 500 C. The rate of heating was maintained at 10 C/hour. The sample prepared by Procedure I showed a total loss of about 14 percent. The loss was complete at about 350 C. The sample prepared by Procedure II showed a total loss of about 18 percent and the loss was complete at about 400 C. The sample prepared by Procedure III, however, showed a continuous loss in weight up to the heating maximum (i.e., 500 C) and the total loss up to 500 C was found to be 22 percent.

### Melting of Gels and Conversion to Glasses

The gel powders obtained after initial heat treatment up to 500 C were melted in a vertical-type furnace at different temperatures and times. The results of these melting experiments with gels obtained after two different heat treatment schedules have been summarized in Tables 15 and 16. Based on the results of melting experiments, efforts were directed towards the preparation of glass samples involving the least amount of heat treatment, and the lowest melting temperatures and times. One batch was melted in a fused silica crucible in order to avoid contamination due to the dissolution of platinum. Results of this work are shown in Table 17.

### Preparation of Glass Samples

Glass samples melted in crucibles were core-drilled using a 3/4 inch drill and annealed for an additional 2 hours at 580 C. All samples used for Rayleigh Scattering studies were polished in kerosene to a path length of 1 cm.

TABLE 15. MELTING OF GELS DRIED BY 48 HOURS HEATING SCHEDULE  
(HEAT TREATMENTS WERE DONE UNDER AMBIENT ATMOSPHERE)

Gel Preparation Procedure	Temperature (C)	Soaking Time (Hours)	Appearance
2-I	800	4	Shows sign of melting, black
	1000	4	Black melt
	1000	8	Black particles in the melt
	1000	24	Some grey particles in the melt
	1200	2	Some grey tinge in the other- wise clear melt
	1200	4	Clear melt
2-III	800	4	Shows sign of melting, black
	1000	4	Black melt
	1000	8	Black particles in the melt
	1000	24	Black particles in the melt
	1200	2	Some grey particles in the melt, otherwise clear melt
	1200	4	Clear melt

TABLE 16. MELTING OF GELS DRIED BY 200 HOURS HEATING SCHEDULE  
(HEAT TREATMENTS WERE DONE UNDER AMBIENT ATMOSPHERE)

Gel Preparation Procedure	Temperature (C)	Soaking Time (Hours)	Appearance
2-II	1000	4	Black particles in the melt
	1000	8	Black particles in the melt
	1000	24	Black particles in the melt
	1200	2	Some grey particles
	1200	4	Clear melt
2-III	1000	4	Black particles in the melt
	1000	8	Black particles in the melt
	1000	24	Black particles in the melt
	1200	2	Some grey particles
	1200	4	Clear melt

TABLE 17. MELTING DATA OF COMPOSITION 2 GEL GLASSES TO BE USED FOR RAYLEIGH SCATTERING STUDIES

Gel Preparation Procedure	Gel Powder Thermal Treatments	Melting Procedures	Appearance of Melt
I	IR dry, 48 hrs 150 C-48 hrs	1200 C-5 hrs uncovered	Grayish-black, no bubbles
I	70 C, RH 95%-24 hrs IR dry, 48 hrs heating schedule 1	1200 C-4 hrs covered	Black, no bubbles
I	70 C, RH 95%-24 hrs IR dry, 48 hrs heating schedule 1	1300 C-4 hrs uncovered	Clear, slight bluish tint, no bubbles
II	IR dry, 48 hrs	1000 C-2 hrs uncovered	Clear, many small bubbles
II	IR dry, 48 hrs	1100 C-2 hrs* uncovered	Clear, no bubbles
II	IR dry, 48 hrs	1000 C-2 hrs 1100 C-2 hrs uncovered	Clear, few small bubbles
II	IR dry, 48 hrs 150 C-48 hrs	1000 C-2 hrs* uncovered	Clear, no bubbles
II	IR dry, 48 hrs heating schedule 1	1200 C-4 hrs covered	Clear, few bubbles
II	IR dry, 48 hrs 150 C-48 hrs	1000 C-1 hr*	Clear, bubbles
Conventional batch	IR dry, 49 hrs heating schedule 1	1200 C-4 hrs covered	Clear, no bubbles

\*Melted in a fused silica crucible.

IR = Infrared.

### Rayleigh Scattering Experiments

Glass samples to be used in Rayleigh Scattering studies were sent to the Vitreous State Laboratory of the Catholic University of America in Washington, D.C. for investigation. The thermal history of the samples sent for Rayleigh Scattering studies are shown in Table 18. Three of the glasses were made by the sol-gel technique and the fourth was made by the conventional technique described previously.

The purpose of the examination was to determine the relative levels of Rayleigh Scattering in these glasses and to correlate these results with the method of preparation of each sample. An approximate Rayleigh Scattering attenuation coefficient was also determined for the glasses by making a comparison of the absolute scattering intensity found in these glasses with a standardized fused silica reference.

The method of making the scattering measurements was that originally suggested for glasses by Rich and Pinnow<sup>(6)</sup> and used by Schroeder, et al<sup>(7)</sup> to examine a number of optical glasses. In brief, that method is to measure the Landau-Placzek ratio,  $R_{LP}$ , for the samples.  $R_{LP}$  is defined as  $I_R/2I_B$  where  $I_R$  and  $I_B$  are the Rayleigh and Brillouin intensities respectively. In making the measurement the sample is illuminated by a focused laser beam and the light scattered at  $90^\circ$  is collected by a collimating lens. The light is spectrum analyzed by a Fabry Perot.

TABLE 18. THERMAL HISTORY OF THE SAMPLES SENT TO NAVAL RESEARCH  
LABORATORY FOR RAYLEIGH SCATTERING STUDIES

Sample Number	Gel Preparation Procedure	Thermal Treatment of Gels	Melting Procedures
1	2-I	Humidity treatment at 70 C and RH-95%/24 hrs IR dry/48 hrs, Heated to 500 C/48 hrs heating schedule	1300 C/4 hrs (uncovered) Annealed at 580 C/2 hrs
2	2-II	IR dry/48 hrs 150 C/48 hrs	1000 C/2 hrs* (uncovered) Annealed at 580 C/2 hrs
3	2-II	Humidity treatment at 70 C and RH-95%/12 hrs IR dry/48 hrs Heated to 500 C/48 hrs heating schedule	1200 C/4 hrs (covered) Annealed at 580 C/2 hrs
4	Conventional Batch	IR dry/48 hrs Heated to 500 C/48 hrs heating schedule	1200 C/4 hrs (covered) Annealed at 580 C/2 hrs

\* Melted in a fused silica crucible.



PART III. GEL-DERIVED GLASSES FOR STUDYING PHASE SEPARATION  
BEHAVIOR (EXPERIMENTAL RESULTS)

Composition 3:  $\text{SiO}_2:60$ ;  $\text{B}_2\text{O}_3:30$ ;  $\text{Na}_2\text{O}:10$  (weight percent) was chosen because the liquid-liquid immiscibility temperature had been determined by Haller et al<sup>(8)</sup>, and the composition is well within the liquid-liquid immiscibility zone. Gel preparation was based on Procedures 3-I and 3-II. The gel preparation procedures are briefly described below.

Gel Preparation Procedures

Procedure 3-I

Starting Chemicals: Tetraethyl Orthosilicate  
Boric Acid  
Sodium Methylate

The sequence of the steps used for the preparation of the gel was as follows:

- (1) Mixing of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  with  $\text{C}_2\text{H}_5\text{OH}$ .
- (2) Partial hydrolysis with acidified water at 40 C. The molar ratio of water to  $\text{Si}(\text{OC}_2\text{H}_5)_4$  was 0.2.
- (3) Addition of boric acid dissolved in methanol.
- (4) Addition of sodium methylate diluted with methanol.
- (5) Addition of water-ethanol mixture to initiate gelation. The molar ratio of water to  $\text{Si}(\text{OC}_2\text{H}_5)_4$  at the end was 3.5. The gelation occurred rapidly.

Procedure 3-II

Starting Chemicals: Tetraethyl Orthosilicate  
Boric Acid  
Sodium Nitrate

The sequence of the steps used for the preparation of gels was as follows.

- (1) Mixing of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  with  $\text{C}_2\text{H}_5\text{OH}$ .
- (2) Partial hydrolysis with acidified  $\text{H}_2\text{O}$  at 40 C.  
The molar ratio of water to  $\text{Si}(\text{OC}_2\text{H}_5)_4$  was 0.4.
- (3) Addition of boric acid dissolved in methanol.
- (4) Addition of sodium nitrate dissolved in excess water. The molar ratio of water to  $\text{Si}(\text{OC}_2\text{H}_5)_2$  was 5.2.
- (5) Gelation achieved overnight.

#### Drying and Melting

The gels were dried under an infrared lamp for 48 hours, and were placed in an oven at approximately 150 C for several days. The gel powders prepared by Procedure 3-I were heated slowly to 350 C and held there for 5 hours. The temperature was then raised to 500 C and held there for approximately 16 hours. The gel powders were then heated quickly to 1200 C and held at that temperature for 6 hours. A bubble-free glass patty was poured and annealed at 580 C for 1 hour. The gel powders prepared by Procedure 3-II were dried for 48 hours under an infrared lamp and placed in an oven at approximately 150 C for several days. A clear bubble-free glass patty was poured and annealed at 580 C for 1 hour.

#### Microstructural Studies

The glass samples obtained by the melting of Composition 3 gel powders and conventional glass batches were sent to the Jet Propulsion laboratory for small angle x-ray scattering studies of phase separation behavior.

The microstructures of the glasses were also observed by SEM. The micrographs of the various samples after different heat treatments are shown in Figures 3 through 8.

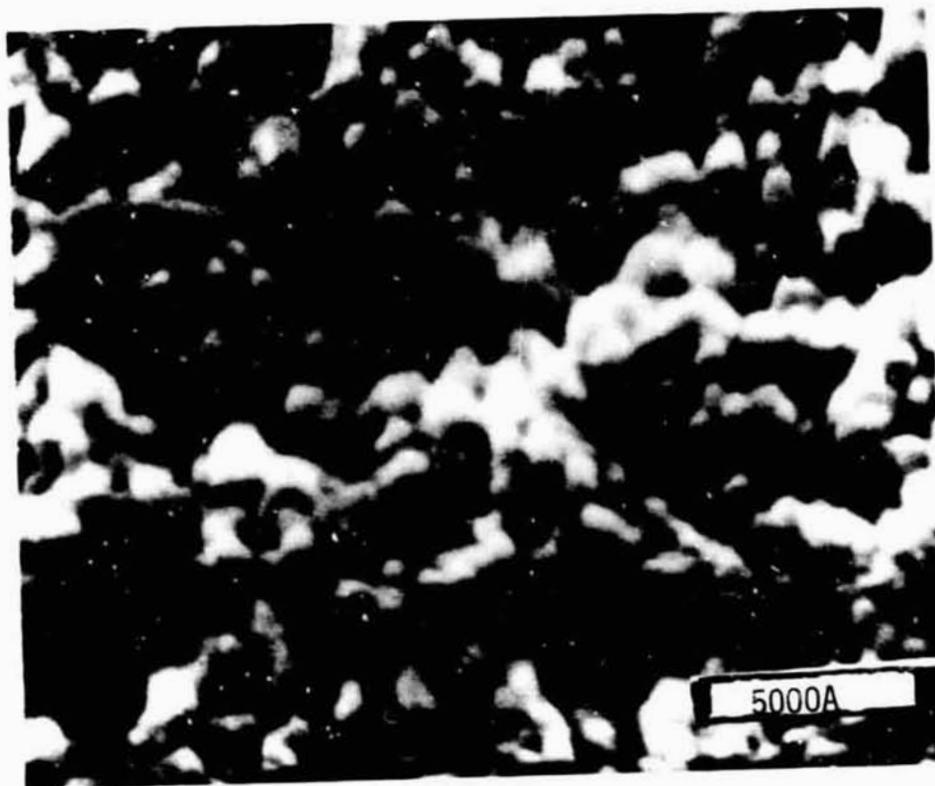


FIGURE 3. SCANNING ELECTRON MICROGRAPH OF THE GLASS  
OBTAINED FROM THE GEL PREPARED BY  
PROCEDURE 3-I WITHOUT ANY HEAT TREATMENT

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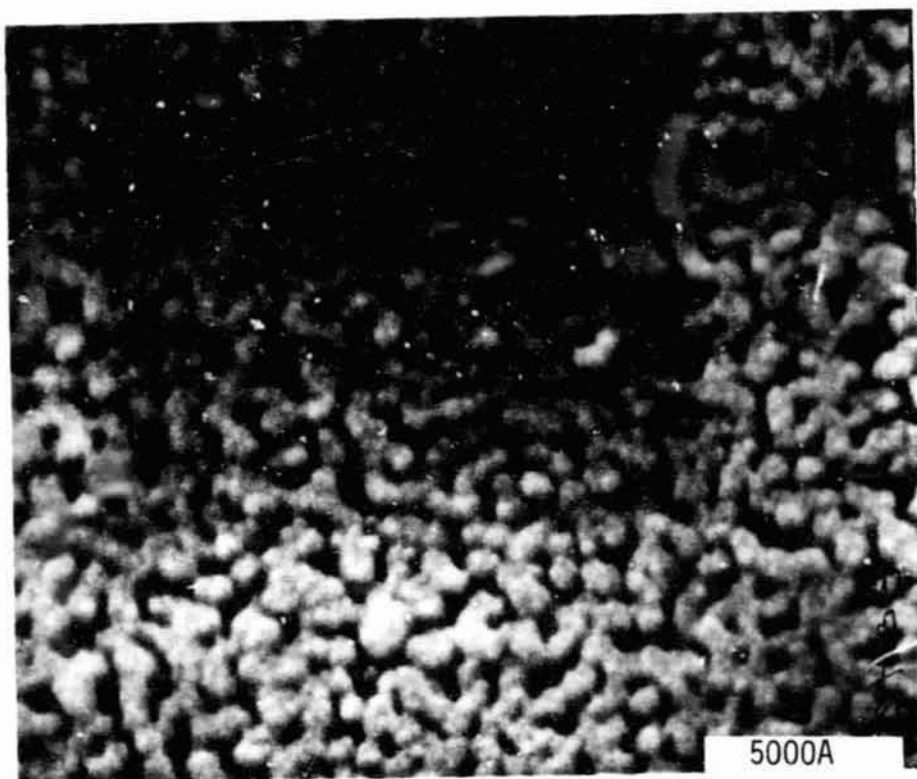


FIGURE 4. SCANNING ELECTRON MICROGRAPH OF THE GLASS  
OBTAINED FROM THE GEL PREPARED BY  
PROCEDURE 3-I AFTER HEAT TREATMENT AT  
600 C FOR 4 HOURS

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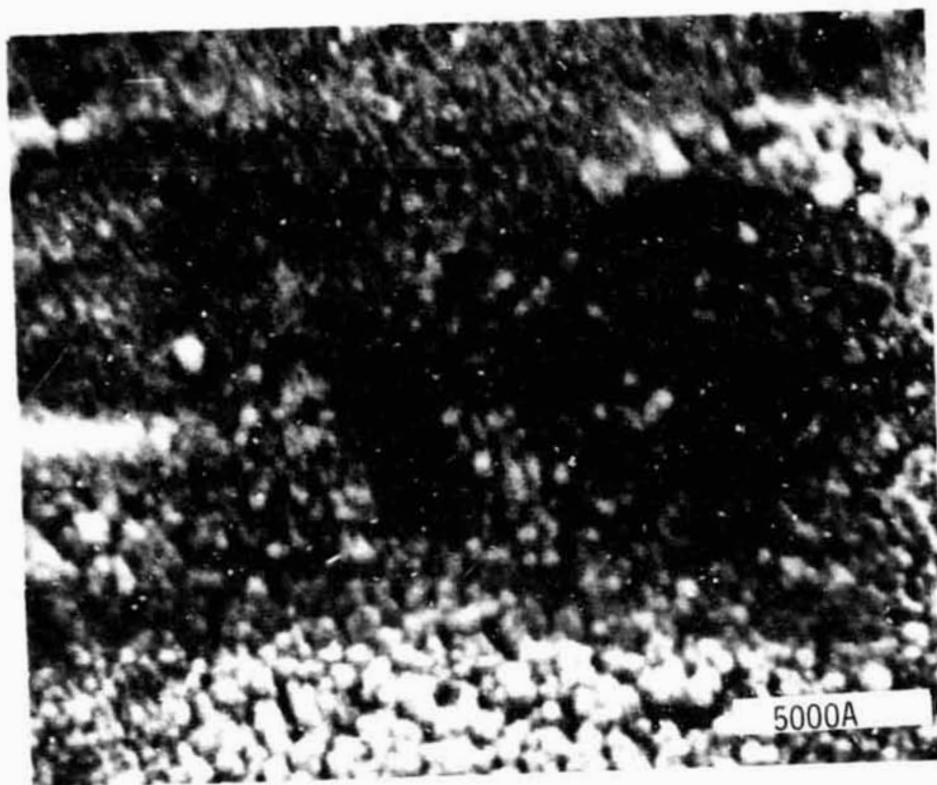


FIGURE 5. SCANNING ELECTRON MICROGRAPH OF THE GLASS  
OBTAINED FROM THE GEL PREPARED BY  
PROCEDURE 3-II WITHOUT ANY HEAT TREATMENT

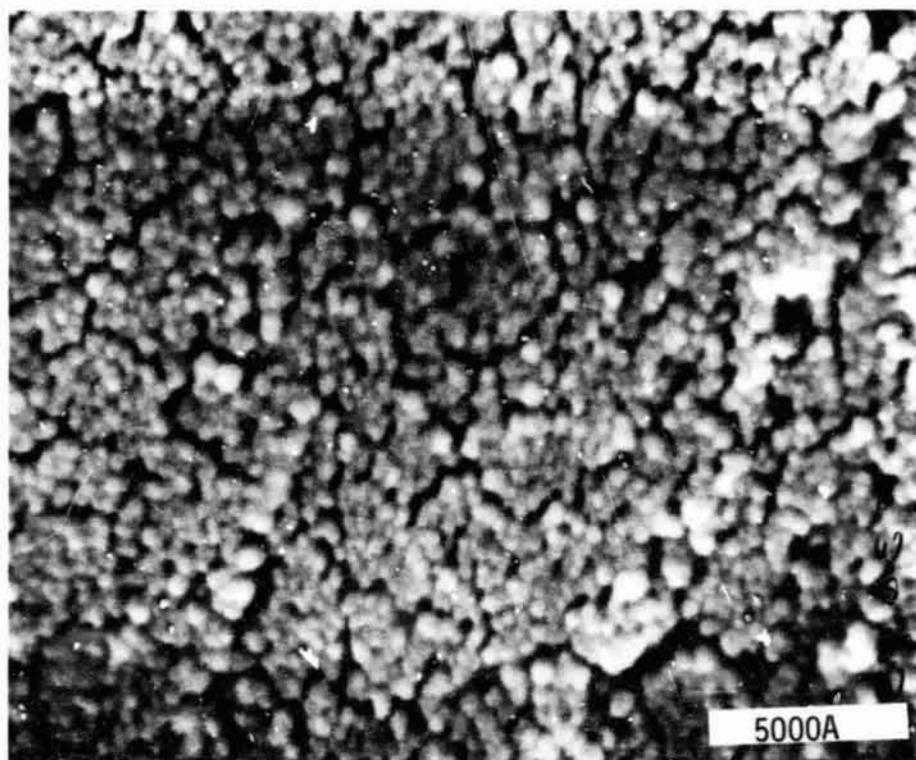


FIGURE 6. SCANNING ELECTRON MICROGRAPH OF THE GLASS  
OBTAINED FROM THE GEL PREPARED BY  
PROCEDURE 3-II AFTER HEAT TREATMENT AT  
600 C FOR 4 HOURS

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FIGURE 7. SCANNING ELECTRON MICROGRAPH OF THE GLASS  
PREPARED FROM THE CONVENTIONAL GLASS  
BATCH, WITHOUT ANY HEAT TREATMENT

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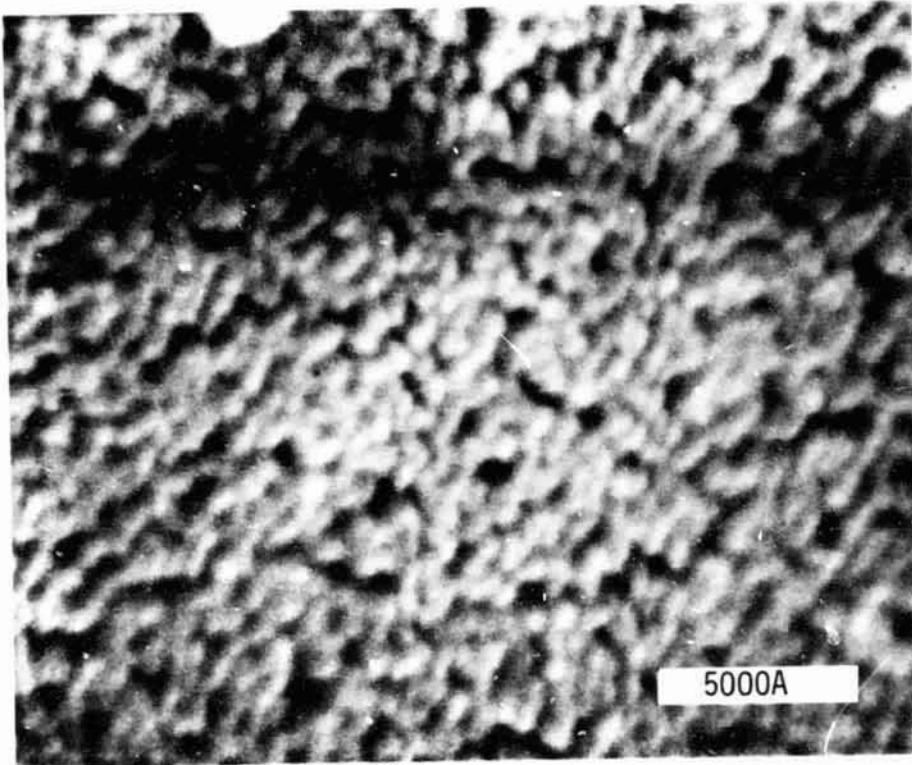


FIGURE 8. SCANNING ELECTRON MICROGRAPH OF THE GLASS  
PREPARED FROM THE CONVENTIONAL BATCH  
AFTER HEAT TREATMENT AT 600 C FOR 4 HOURS



## DISCUSSION OF TOTAL PROGRAM

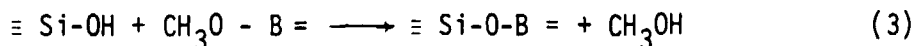
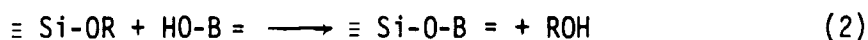
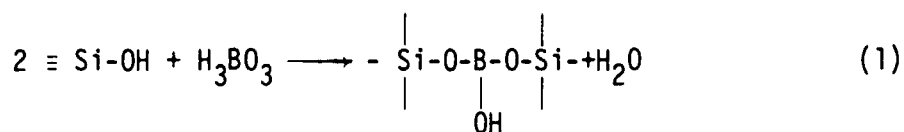
### Preparation of Gels

The formation of the condensed polysilicates and subsequent gelation is the result of a complex sequence of hydrolysis and condensation reactions. The complexity increases in a system with components having different reactivity and solubility. Gelling is controlled by process parameters such as chemical nature of alkoxides and other reactants, molecular ratio of water to alkoxides, the presence of catalysts and pH of the medium, temperature, concentration of reactants, and the nature of solvents.

In this multicomponent system having reactants of markedly different chemical nature, it is extremely difficult to change the process parameters independently of each other<sup>(9)</sup>. Moreover, the addition of aqueous solution such as sodium nitrate and sodium acetate which are insoluble in alcohol should be considered in the context of the liquid-liquid immiscibility existing in the  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and  $\text{H}_2\text{O}$  system. The possibility of segregating water-soluble phases under certain experimental conditions should be investigated. To homogeneously incorporate a high proportion of  $\text{Na}^+$  ions (which is not a network former) into a gel structure is complex and difficult.

In Procedure I, all reactants are soluble in alcohols and it is presumed that a homogeneous solution of the molecular species was obtained at the final stage. However, the sequence of reactions may be postulated as follows: in acid medium, the hydronium ion attacks the polar  $\equiv \text{Si}-\text{OC}_2\text{H}_5$  bond and forms  $\equiv \text{Si}-\text{OH}$  groups. However, in this type of nucleophilic displacement reactions the reactivity decreases as more groups on the silicon atom are displaced. The polysilicate is formed through condensation of silanol groups;  $\text{SiOH}$ ; or silanol and alkoxy groups ( $\equiv \text{Si}-\text{OC}_2\text{H}_5$ ). The further attack of  $\equiv \text{Si}-\text{OC}_2\text{H}_5$  bond in the polysiloxane by  $\text{H}_2\text{O}$  might also be hindered by the steric effect of ethoxy groups. The hydrolysis of ethylsilicate is thus controlled by the

electronic and steric effects developed during hydrolysis. Hence the formation of low-molecular-weight molecules takes place under mild conditions of hydrolysis at room temperatures and with a small proportion of  $H_2O$ . Recent work of Peace, et al<sup>(10)</sup> on the hydrolysis alkoxy silanes suggests that the polymers at the initial stage of hydrolysis might have a ring structure--perhaps a dimer with two connected rings each containing four silicon atoms. Boric acid itself or methyl borate  $B(OCH_3)_3$  which could form by the reaction of methanol with boric acid can react with silanol or alkoxy groups and form Si-O-B = bonds in the following way:



An advantage of the addition of boric acid is that a certain amount of water is liberated during the reaction of  $H_3BO_3$  either with silanol groups or with alcohols, and this water produced in situ could effectively induce further hydrolysis without addition of free  $H_2O$ . After subsequent addition of sodium methoxide solution, the pH of the solution increases above 9, and consequently the mechanism and kinetics of hydrolysis and polycondensation changes. Moreover, sodium methoxide being highly susceptible to hydrolysis (e.g.,  $NaOCH_3 + H_2O \longrightarrow NaOH + CH_3OH$ ) produces OH groups which enhance the polycondensation and growth of the polymeric particles. Subsequently, the solution absorbs sufficient water from the atmosphere or when free water is added, the gelation occurs rapidly. The observed increased gelling rate with increased proportion of water at the initial stage of hydrolysis suggest that any free water remaining before adding sodium methoxide causes the generation of hydroxyl groups which enhance the gelation. The decreased gelling time with increased  $NaOCH_3$  and with increased humidity also indicates the hydrolytic reaction of the  $NaOCH_3$  and the catalytic activity of OH groups. The incorporation of  $Na^+$  ions into the gel structures might

take place as follows<sup>(8)</sup>: NaOH generated by the hydrolysis of NaOCH<sub>3</sub> might react with Si-OC<sub>2</sub>H<sub>5</sub> group to produce SiONa. Sodium methoxide having strong ionic character might undergo ion exchange with H<sup>+</sup> ion of silanol groups at high pH and may produce SiONa. A secondary reaction forming tetra-coordinated boron of the type Na[B(OCH<sub>3</sub>)<sub>4</sub>] might take place when free or partially hydrolyzed B(OCH<sub>3</sub>)<sub>3</sub> reacts with NaOCH<sub>3</sub>.

In Procedure II, the initial reactions of tetraethoxysilane with boric acid are anticipated to be similar to those described for Procedure I. However, the addition of higher proportion of water and of acids would lead to more complete hydrolysis of ethoxysilane. The polymer molecules contain less unreacted ethoxy groups, and the solution shows little tendency to gelation. Sodium nitrate additions, unlike NaOCH<sub>3</sub> or sodium acetate, do not increase the pH. Consequently, the gelling time is long. Sodium nitrate, not being reactive to other reactants and being insoluble in alcohols, segregates in the aqueous phase and precipitates as NaNO<sub>3</sub> as the gels dry, as evidenced by the x-ray diffraction results. The heat treatment at 500 C or above decomposes the nitrate and reactive Na<sub>2</sub>O forms; thus, the crystallinity decreases with the heat treatment. However, excess water and the low gelation rate are beneficial for hydrolyzing alkoxy groups and subsequent removal of organics.

In Procedure III, the initial stage of the hydrolytic reactions in the presence of a high proportion of water and acid is similar to that of Procedure II. Consequently, the hydrolysis is more complete and the solution being at low pH ( $\leq 2$ ) shows less tendency to gel. sodium acetate solution is added, the gelation occurs due to the high concentration of OH ions present in sodium acetate solution; the pH of the solution increases to higher gelling rate region and gelation occurs rapidly.

The surface areas of gels produced from the low pH solution is large because, in strongly acid medium, the polymeric particles cannot grow; consequently, gels produced from submicron particles have higher surface areas. The significant difference in the surface areas of the gels prepared by the different procedures can be interpreted in terms

of the effect of pH on the size of the particles. When the gelation is done with solution of low pH ( $\leq 2$ ) the particle sizes are smaller, and, consequently, the pore sizes are finer. The incorporation of  $\text{Na}^+$  ions into the gel structure might occur either by the reaction of NaOH produced by the hydrolysis of sodium acetate with  $\text{Si-OC}_2\text{H}_5$  group or by the exchange of  $\text{H}^+$  ions of the silanol groups with  $\text{Na}^+$  ions of acetate solution. But a portion of  $\text{Na}^+$  ions might remain in the water phase and could produce a nonuniform distribution of  $\text{Na}^+$  ions in the gels.

The results of the infrared and Raman spectroscopic studies of glasses made from the different gels and having different melting histories (e.g., time and temperature of melting) indicate that the molecular structures of the glasses made from the gels prepared by different procedures and melted at lower temperatures ( $\leq 1000^\circ\text{C}$ ) are not identical. However, the melting at higher temperatures ( $1100\text{--}1200^\circ\text{C}$ ) appears to be sufficient to give an equilibrium melt for each gel. Studies on glasses melted at lower temperatures (e.g.,  $700\text{--}1000^\circ\text{C}$ ) may throw some light on the process of approaching an equilibrium melt.

#### Removal of Organics From Gels

The "as prepared" gels may be considered as a solid character in which macromolecules are dispersed in a solvent and somehow constitute a coherent structure. Thus, it contains the structural skeleton of the silicate network; unreacted alkoxy groups chemically bonded to the silicate network; free solvents, like alcohols and water; and alcohols and water absorbed to the silicate structure. Hence, the removal of these organic compounds and also inorganic radicals, such as nitrates, is a complex phenomenon and is related to the structure and morphology of the gels which in turn is related to the chemical nature of the gel precursors used in the gel preparation procedures as well as the thermochemical nature of the gel precursors.

The thermal treatment of gels containing alcohols/ethers/water would normally involve volatilization of these constituents at all temperatures with the maximum rate of vaporization near their boiling points. This phenomenon is, however, related to the balance between

the rate of diffusion of the solvents/water from inside the gel structure to the surface of the gel and the rate of evaporation of solvents/water from the gel surface to the surrounding atmosphere at the equilibrium temperature. The dynamic nature of the heat treatment procedure establishes an imbalance between the above two rates and, as a result, evaporation of solvents/water may continue to take place at temperatures beyond their boiling ranges. Besides, if the solvents/water are chemically bound or chemisorbed to the gel structure, evaporation temperatures would be higher. Moreover, during the thermal treatment the initial densification of the gel structure takes place resulting in the formation of increasing number of closed pores. The presence of solvents (e.g., alcohols, ethers, etc.) in the closed pores make them inaccessible to the surrounding atmosphere even at considerably higher temperatures. Therefore, at somewhat higher temperatures thermochemical reactions of the organic solvents present in the closed pores and organic radicals (connected to the gel structure) may take place resulting in the formation of carbon. Also, the thermochemical nature of the gel precursors either alone or in combination may result in the deposition of carbon due to incomplete hydrolysis and polymerization (hydrolytic polycondensation). It is to be noted that pyrolyses of alcohols, aliphatic ethers, acetic acid and ester give gaseous mixtures of approximately the same composition (methane, ethane, ethylene, acetylene carbon monoxide, etc.). During pyrolysis of ethylene and acetylene the residue  $[\text{CH}_2 \equiv]$ ,  $[\text{HC} \equiv]$  are considered to be formed by direct rupture of the carbon-to-carbon bonds. These residues may become dehydrogenated further into carbon. The problems associated with the deposition of carbon during initial thermal treatment of gels are:

- The complete removal of carbon needs higher melting temperature and longer soaking time.
- Complete removal of bubbles (from gel-derived glass) needs longer soaking time.

It would therefore appear that the conversion of gel into glass at lower temperature essentially depends upon the successful removal of organics during preliminary heat treatment or drying of gels. Proper selection of heating rate and the furnace atmosphere are to be considered

for the thermal treatment of gels. In the present investigation the behavior of the gels towards thermal treatments were studied with gels prepared by two different procedures, Procedure I and III. The thermal treatment consisted of humidity treatments, heating in steps, slow rate of heating and moistening the gel during heating under different furnace atmospheres. The results of the present work indicate that the thermal treatment of gels in a humidity chamber just after preparation has beneficial effect on the removal of organics. This suggests that the hydrolysis and increased polymerization can take place in the solid phase. The water vapors react with the unreacted ethoxy groups during the humidity treatment and causes polycondensation. In general, humidity treatment was more beneficial for removing organics in the gels prepared by Procedure I than those prepared by Procedure III. This may be due to the fact that the gel prepared by Procedure III has smaller pore sizes and/or larger number of closed pores.

It is to be noted that it was possible to achieve complete removal of organics in the gels prepared by Procedure II during preliminary heat treatment up to 500 C even without humidity treatment. This may be due to one or all of the following factors:

- Less number of closed pores.
- Comparatively large pore sizes.
- The decomposition of sodium nitrate creates/develops an oxidizing environment inside the gel structure and, as a result, dehydrogenation or thermal cracking of organic molecules or radicals are prevented.

It is to be mentioned that although prolonged humidification of freshly prepared gel followed by soaking the gel with water at elevated temperatures was found to be the most effective method of removing the organics, it was not fully effective in removing the organics completely. Therefore, the presence or formation of closed pores appears to be the single most important factor which makes the complete removal of organics from gels a difficult task.

### Removal of Hydroxyl Groups From Gels

The hydroxyl concentration in a glass is determined by:

- The water content of the raw material.
- The sintering properties of the starting materials.
- The  $H_2O$  partial pressure of the surrounding gas during melting.
- The  $H_2$  partial pressure of the surrounding gas during melting.
- The thermal history of the glass.

Hence, the hydroxyl content in the starting material needs to be reduced by thermal treatment. The following steps were taken for the removal of hydroxyl groups from gel powders of Composition 1.

- Baking in an oven.
- Passing dry  $O_2$  through the porous gels at elevated temperature.
- Passing thionyl chloride ( $SOCl_2$ ) vapor carried by dry oxygen through the porous gels at elevated temperatures.
- Passing carbon tetrachloride ( $CCl_4$ ) vapors carried by dry oxygen through the porous gels at elevated temperatures.
- Subsequent melting of the thionyl chloride treated/ carbon tetrachloride treated gels in air atmosphere.
- Melting of dehydrated gels in nitrogen atmosphere.

The results of the present investigation indicate that:

- The water content of the glasses obtained from two different gels differ significantly.
- The hydroxy. content could be reduced at lower dehydration temperature by passing dry oxygen through a vertical column packed with gel powders.
- Use of thionyl chloride for reducing hydroxyl groups at lower temperatures results in liquid-liquid phase separation. A large liquid-liquid immiscibility<sup>(5)</sup> zone exists in the system  $SiO_2$ - $Na_2O_2$ - $Na_2SO_4$  at 1200 C.

Presumably, during the dehydration treatment thionyl chloride reacts with sodium ion and residual water to form sodium sulfate which causes liquid-liquid separation during melting.

- The presence of a large proportion of sulfur and sodium in the top fluid layer substantiate the explanation suggested. The use of thionyl chloride may not, therefore, be advisable in this system.
- The use of carbon-tetrachloride during dehydration treatment did not cause liquid-liquid separation during melting and was, at the same time, effective in reducing the hydroxyl groups in the glass.
- Melting of dehydrated gels in dry nitrogen atmosphere was found to be very effective in reducing the hydroxyl groups.

### CONCLUSIONS

The following conclusions can be drawn from the results of the present work:

- All three compositions in the soda-borosilicate system can be prepared by three different procedures using three different sources of  $\text{Na}_2\text{O}$ .
- Gels produced by Procedure I and Procedure III are noncrystalline, and remain so after thermal treatment at 600 C for 40 hours, whereas gels prepared by Procedure II using  $\text{NaNO}_3$  are crystalline due to the presence of residual sodium nitrate.
- The removal of organic groups during the thermal treatment below 500 C is related to gel preparation procedures, ambient atmosphere such as humidity and oxygen potential, and the rate of heating. The carbon content of the fired gel can vary from 0.1 percent to 0.6 percent by weight depending on the preparation procedure.



- The rate of removal of carbon from the glass during the melting depends on the gel preparation procedures and thermal treatment before melting. The removal of carbon from the gel prepared by Procedure II is most rapid, whereas the removal is most sluggish with the gel prepared by Procedure III.
- The rates of removal of carbon and the bubbles were also a function of temperature and time of melting in an air atmosphere.
- Molecular structures of the glasses melted at lower temperatures ( $\leq 1000$  C) are not identical; however, the melting at higher temperatures 1100-1200 C appears to give an equilibrium melt from the different gels.
- Gel preparation procedures can be improved to get higher homogeneity.
- Microstructures of glasses obtained from gels prepared by different procedures are different.
- The water content of glasses obtained from the two different gels differs significantly.
- The dehydration treatment reduces the hydroxyl content of the glass.
- The removal of hydroxyl groups from gel powders by the treatment with thionyl chloride vapor causes phase separation in the glass during melting. The reason for this phase separation is most likely due to the formation of sodium sulfate during the thionyl chloride treatment. Hence, the thionyl chloride treatment procedure should be critically analyzed before further continuation.
- The vertical column for dehydration is more effective than the horizontal set-up used previously for the dehydration treatment.

- Bubbling dry nitrogen (dewpoint approximately -59 C) through the melt greatly reduces the hydroxyl content of the glass.
- Procedure II gel powders can be used to produce glass samples for Rayleigh scattering by employing less thermal treatments and lower melting temperatures and times.
- Glass samples for Rayleigh Scattering can be prepared by melting in a fused silica crucible at 1000 C for 1 hour if appropriate procedures are followed.
- Results of Rayleigh Scattering studies indicate that the homogeneity of glasses prepared by the gel technique is much better than that of glasses made by the conventional technique.

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APPENDIX

Experimental Details of Gel Preparation Procedures

Gel Preparation Procedures for Composition 1:

SiO<sub>2</sub>:60, B<sub>2</sub>O<sub>3</sub>:15, Na<sub>2</sub>O:25 (weight percent)

Gel Preparation Procedure 1-I

The sequence of steps used for the preparation of the gel was as follows:

1. Tetraethyl orthosilicate was mixed with half its volume of anhydrous ethanol and stirred for about five minutes.
2. The solution was heated to 40 C and hydrolyzed with 0.23 mol water per mol Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> acidified with 0.0004 mol HCl per mol Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>. A small amount of acetylacetone (3 ml/100 ml Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) was added after the addition of acidified water. The solution was stirred at 40 C for a half hour after the addition of water. The pH of the solution was 5.
3. Boric acid dissolved in boiling anhydrous methanol (30 g/100 ml) was added to the above solution at 40 and stirred for ~ 1 hour. The pH of the solution was 6 at this stage.
4. A solution of sodium methylate (prepared by mixing commercially available 30 percent NaOCH<sub>3</sub> in methanol with half its volume of anhydrous methanol) was added to the above solution at 40 C and stirred for 45 minutes. The pH of the solution was about 10.
5. Finally, a mixture of water and ethanol (1:4 ratio) was added to the solution. The amount of water added was 5.8 mols per mol (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>). The solution gelled within five minutes on addition of the alcohol water mixtures.

Gel Preparation Procedure 1-II

The sequence of steps used for the gel preparation was as follows:

1. Tetraethyl orthosilicate, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> was mixed with half its volume of anhydrous ethanol and stirred for about five minutes.
2. The solution was heated to approximately 40 C and hydrolyzed with 0.5 mol water per mol Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> acidified with 0.0004 mol HCl per mol (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>). The solution was stirred for a half hour at about 40 C after the addition of water.

3. Boric acid dissolved in boiling anhydrous methanol (30 g/100 ml) was added to the solution at 40 C and stirred for about 1 hour. The pH of the solution was about 5.

4. Finally, an aqueous solution of sodium nitrate (~ 18 g/100 ml) was added to the mixture. The proportion of water was 20 mols per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The solution was then evaporated till gelation took place.

#### Gel Preparation Procedure 1-III

The sequence of steps used for the gel preparation was as follows:

1. Tetraethyl orthosilicate was mixed with half its volume of anhydrous ethanol and stirred for about five minutes.
2. The solution was heated to 40 C and hydrolyzed with 11 (eleven) mols of water per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$  in the presence of die nitric acid. The pH of the solution was about 2 during hydrolysis. The solution was stirred for half hour at 40 C after the addition of water.
3. Trimethyl corate was added to the mixture at 40 C and stirred for 45 minutes.
4. Finally, one molar aqueous solution of sodium acetate was added to the above solution and stirred for 45 minutes. The pH of the solution was 6. Gelation took place after 30 minutes.

#### Gel Preparation Procedures for Composition 2;

$\text{SiO}_2:55$ ,  $\text{B}_2\text{O}_3:25$ ,  $\text{Na}_2\text{O}:20$  (weight percent)

#### Gel Preparation Procedure 2-I

The sequence of steps used for the preparation of the gel was as follows:

1. Tetraethyl orthosilicate was mixed with three times its volume of anhydrous ethanol and stirred for about five minutes.
2. The solution was heated to 40 C. A small amount of HCl [0.0002 mol/mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ] was added; followed by the addition acetylacetone [5 ml/100 ml  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ]. The solution was stirred for about 1 hour at

- 40° C for partial hydrolysis of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The pH of the solution was 3.6. The solution was cooled to ambient temperature.
3. Boric acid dissolved in boiling anhydrous methanol (30 g/100 ml) was added and stirring was continued for about 2 hours. The pH of the solution was 3.6.
4. A solution of sodium methylate (prepared by mixing commercially available 30 percent  $\text{NaOCH}_3$  in methanol with an equal volume of anhydrous methanol) was added and stirred for 45 minutes. The pH of the solution was about 10.
5. Finally, a requisite amount of anhydrous ethanol was added to obtain a concentration of approximately 40 g silica per liter of the solution. After addition of anhydrous ethanol the solution was stirred for a further period of 30 minutes. The solution gelled in 3 hours.

#### Gel Preparation Procedure 2-II

The sequence of steps used for the preparation of the gel was as follows:

1. Tetraethyl orthosilicate was mixed with three times its volume of anhydrous ethanol and stirred for about 5 minutes.
2. The solution was heated to 40 C. Approximately 0.5 mol water per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$  acidified with 0.0004 mol HCl per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$  was added. The solution was stirred for about one hour at 40 C for partial hydrolysis of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The pH of the solution was 2.8.
3. Boric acid dissolved in boiling anhydrous methanol (approximately 30 g/100 ml) was added to the partially hydrolyzed tetraethyl orthosilicate and stirring continued for 1 hour at 40 C. The pH of the solution was 2.4.
4. Finally, a dilute aqueous solution of sodium nitrate (approximately 17 g/100 ml) was added to the mixture and stirring was continued for 3 hours. The pH was 3.2. The solution was left at ~ 40 C for about 3 days to form the gel.

Gel Preparation Procedure 2-III

The sequence of steps used for the preparation of the gel was as follows:

1. Tetraethyl orthosilicate was mixed with three times its volume of anhydrous ethanol and was stirred for about 5 minutes. The solution was heated to 40 C and partially hydrolyzed with one mol of water per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$  acidified with 0.02 mol HCl per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The solution was stirred for 1 hour at 40 C. The pH of the solution was 0.2.
2. The solution was cooled to room temperature and the requisite amount of trimethyl borate was added. The mixture was stirred for 3 hours at room temperature. The pH of the solution was 0.4.
3. Finally, a buffer solution of 0.5M Sodium Acetate (prepared by dissolving Crystalline Sodium Acetate in water to which acetic anhydride was added) was added and the solution stirred for 2 to 3 minutes. The pH was 5.5. The solution gelled in about 1 hour.

Gel Preparation Procedures for Composition 3

$\text{SiO}_2:55$ ,  $\text{B}_2\text{O}_3:25$ ,  $\text{Na}_2\text{O}:20$  (weight percent)

Gel Preparation Procedure 3-I

The sequence of steps used for the preparation of the gel was as follows:

1. Tetraethyl Orthosilicate  $\text{Si}(\text{OC}_2\text{H}_5)_4$  was mixed with half its volume of anhydrous ethanol and stirred for about 5 minutes.
2. The solution was heated to 40 C and hydrolyzed with 0.2 mol of water per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$  acidified with 0.0004 mol HCl per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The solution was stirred at 40 C for a period of 45 minutes. A small volume of acetylacetone [2 ml/100 ml  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ] was added after the addition of acidified water.
3. Boric acid dissolved in boiling anhydrous methanol (30 g  $\text{H}_3\text{BO}_3$ /100 ml MeIhavol) was added to the partially hydrolyzed  $\text{Si}(\text{OC}_2\text{H}_5)_4$  solution at 40 C and stirred for 20 minutes. The pH of the solution was 4.5. The solution was cooled to ambient temperature.



3. A solution of sodium methylate (prepared by mixing commercially available 30 percent sodium methylate in methanol with an equal volume of anhydrous methanol) was added to the above solution and stirred. The pH of the solution was 6.
4. Finally, 3.3 mols  $\text{H}_2\text{O}/\text{mol Si}(\text{OC}_2\text{H}_5)_4$  was added in the form of alcoholic solution. The solution was prepared by mixing water and alcohol in equal volumes. The molar ratio of water to  $\text{Si}(\text{OC}_2\text{H}_5)_4$  at the end was 3.5. The gelation occurred rapidly.

#### Gel Preparation Procedure 3-II

The sequence of steps used for the preparation of the gel was as follows:

1. Tetraethyl Orthosilicate,  $\text{Si}(\text{OC}_2\text{H}_5)_4$  was mixed with half its volume of anhydrous ethanol and stirred for about 5 minutes.
2. The solution was heated to 40 C and hydrolyzed with 0.4 mol water per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$  acidified with 0.0002 mol HCl per mol  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The solution was stirred at 40 C for half hour. The pH of the solution was about 4.
3. Boric acid dissolved in boiling anhydrous methanol (22 g  $\text{H}_3\text{BO}_3/100$  ml methanol) was added to the partially hydrolyzed  $\text{Si}(\text{OC}_2\text{H}_5)_4$  solution at 40 C and stirred for a half hour. The pH of the solution was 4.
4. 13.5 percent aqueous solution of  $\text{NaNO}_3$  was added to the above solution and stirred. The molar ratio of water to  $\text{Si}(\text{OC}_2\text{H}_5)_4$  was 5.2 at this stage. The solution was heated to 75 C with continuous stirring. Gelation took place in 2-1/2 hours.

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# SOL-GEL PROCESSES IN GLASS SCIENCE AND TECHNOLOGY

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The scientific and technological significance and importance of the sol-gel processes are evaluated. Two methods for preparing gels in the silicate systems are described. The first method is based on gelling colloidal silica sol; the second method, on the polymerization of alkoxysilane with metal alkoxides or metal salts to produce multicomponent noncrystalline inorganic gels with network structures. The physico-chemical principles of gelling processes are discussed in terms of various process parameters. The conversion of gel to glass is described. The structures, microstructures, phase separation and crystallization behavior of gels and gel-derived glasses are discussed in relation to the methods of gel preparation. The advantages associated with the processes are examined and evaluated. Various applications in glass technology are suggested.

## INTRODUCTION

In recent years, sol-gel processes for glass making have gained scientific and technological importance. There are two methods for preparing gels in silicate glass systems. One is based on the gelation of silica hydrosol<sup>(1-3)</sup>, the other is based on the polymerization reaction of alkoxysilane<sup>(2,3,4-10)</sup>.

Earlier research involved gels as starting materials for the silicate phase equilibrium studies<sup>(11)</sup> and the deposition of thin noncrystalline oxide coatings<sup>(12,13)</sup>. In recent years, two aspects of the sol-gel process have stimulated research on the preparation of glasses via the gel route. First is the formation of noncrystalline transparent "glass-like" materials in the multicomponent systems below the glass transition temperature<sup>(5-10)</sup>. Second is the preparation of highly homogeneous glasses using gels as starting materials<sup>(2,3,8)</sup>. Moreover, the phase separation, nucleation and crystallization characteristics of the glasses made from gels are markedly different from those of glass made from a mixture of oxides<sup>(3,8,13)</sup>.

These aspects have scientific and technological significance and importance. The formation of transparent noncrystalline materials by chemical polymerization at temperature below the glass transition temperature raises the question whether these materials should be termed "glass" or not, because the ASTM definition of glass as an "inorganic product of fusion" excludes these types of noncrystalline materials. However, the molecular structure and the microstructure of these "glass-like" materials prepared by this route in multicomponent systems appear to be different from the glass prepared from the oxide melt<sup>(8)</sup>. Because the structures of the gel-derived materials depend on the thermodynamics and kinetics of the polymerization reactions that take place in the sol and gel state at low

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temperatures, whereas the structures of the glass prepared from the melt depend on the thermodynamics and kinetics of the reactions of oxide mixtures in molten and supercooled state.

The prime technological importance of the sol-gel process is that it opens up a possibility of preparing homogeneous, high temperature "glasses" and "glass-ceramics" at low temperature, that are hard to prepare by melting of oxide mixtures. These glasses are hard to prepare by melting oxides because of (a) the high melting temperatures, and (b) a strong tendency to crystallize when cooling through the temperature having maximum crystallization rate. The sol-gel process is particularly suitable for coating deposition and fiber fabrication. Hence, the deposition of high-temperature oxide coatings on substrates at low temperatures, and the fabrication of high-temperature glass and glass-ceramic fibers are of potential technological importance.

In this paper, the following aspects of the sol-gel processes are critically reviewed and discussed: Preparation of Gels, Conversion of Gel to Glass, Microstructure and Structure of Gels and Gel-Derived Glasses, Advantages, and Applications.

## PREPARATION OF GELS

### Gelation of Silica Hydrosol

Method I is based on the principles of colloid science. The essential feature is to disperse the metal compounds into their elementary units in an aqueous solvent. This dispersed phase, called "sol", is then converted into a rigid "gel" by destabilization process. During gelation, the overall medium becomes viscous and is then solidified by a coherent network of particles<sup>(14)</sup>. This is distinctly different from precipitation. Figure 1 indicates the process for preparing glass in the silicate system by this method.

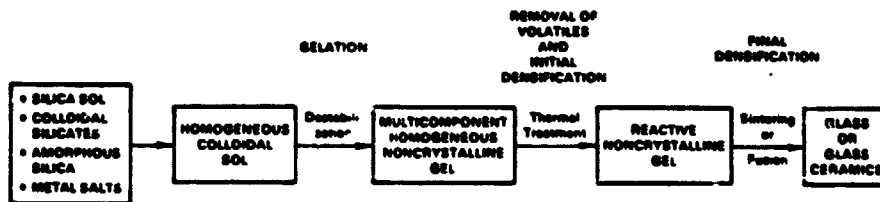
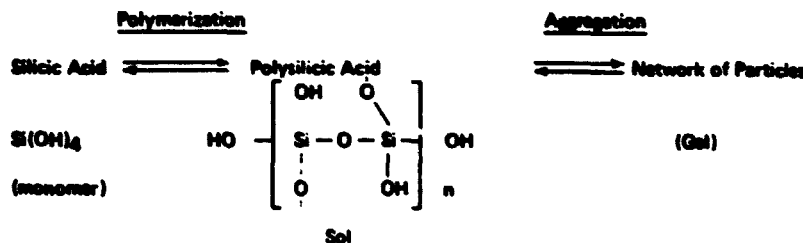


FIGURE 1. SOL-GEL PROCESS FOR GLASS MAKING--FIRST METHOD

The gelling process of silica, which is the main constituent of silicate gel systems can be represented as follows:



The gelling process consists of three stages: polymerization of monomer (silicic acid) to form particles, growth of particles and linking of particles together into branched chains, then networks finally extending throughout the liquid medium, thickening it to gel. However, the conditions leading to the formation and growth of the particles are different from those leading to aggregation or gelation. The factors influencing the gelling process are: pH of the medium and the presence of a catalyst, electrolytes and coagulants, particle size and concentration, temperature<sup>(1-7)</sup>.

The role of pH is extremely important in the rate of gelling of silica sol. In certain pH regions, the sol is fairly stable. The gelling rate of pure silica sol is maximum around pH 5. However, the addition of metal salts, which reduces the overall net repulsion effect, enhances the gelling and coagulation. The metal ions in the +3 and -- oxidation states and of nuclear and rare earth compounds may behave differently as they tend to form a condensed form of small polymeric cations in aqueous solutions<sup>(15)</sup>. For example, a cyclic tetramer of zirconium  $(\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_8)^{8+}$  (10A) which forms initially in a concentrated sol condenses further to form larger (~100A) polynuclear ions<sup>(15)</sup>. These types of polynuclear species might react, under proper experimental conditions, with the colloidal silica to form complex metal silicate species. Hence, the critical step in Method I is to prepare a stable, homogeneous, multicomponent sol, which could destabilize to a homogeneous rigid gel. Konijnendijk, et al, have reported<sup>(2)</sup> the preparation of homogeneous glasses in alkali-borosilicate system prepared via this gel route. Mukherjee, Zarzycki, and Traverse<sup>(3)</sup> prepared homogeneous glass in rare earth silicate system via this gel route. Also Shoup<sup>(16)</sup> has reported the fabrication of monolithic porous silica gel articles, and has subsequently consolidated them to transparent silica bodies at 1400 to 1720 C.

#### Polymerization of Alkoxysilanes and Metal Alkides

Method II is based on the polymerization (hydrolytic polycondensation) of alkoxysilane with other metal alkoxides or with suitable metal salts to produce multicomponent noncrystalline transparent "glass-like" gels with a network like  $\text{Si-O-M-O-Si-}$  where M is a metal atom, such as Al, Ti, or B. A partial hydrolysis of alkoxysilane introduces the active functional groups which react with other reactants to form a polymeric solution which further polymerizes with time and increased temperature to form a rigid gel.

In the polymerization process of organic compounds<sup>(17)</sup>, when the polyfunctional monomers undergo nonlinear condensation and form a gel, the gel point is defined as the stage in the course of polymerization when the concentrate transforms suddenly from a viscous liquid to an elastic gel. At the gel point, the generation of the infinite network commences abruptly and gel polymerization increases rapidly with further condensation. As the degree of polymerization increases

beyond the gel point, the relative proportions of "sol" and "gel" have varied continuously, the larger molecules in the sol being progressively incorporated into the gel.

Mukherjee<sup>(16)</sup> measured the change of viscosity with time of a solution prepared by reacting a mixture of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Al}(\text{OC}_2\text{H}_5)_3$ ,  $\text{B}(\text{OC}_2\text{H}_5)_3$ ,  $\text{Ba}(\text{OC}_2\text{H}_5)_2$  and  $\text{NaOCH}_3$ . A sharp rise of viscosity was observed at the gel point and an abrupt gelation indicating the generation of the infinite network occurred. Presumably, the polymerization reactions of alkylsilane and metal alkoxides under certain conditions might be based on the gelation process mentioned above.

A schematic diagram of the sol-gel process is shown in Figure 2.

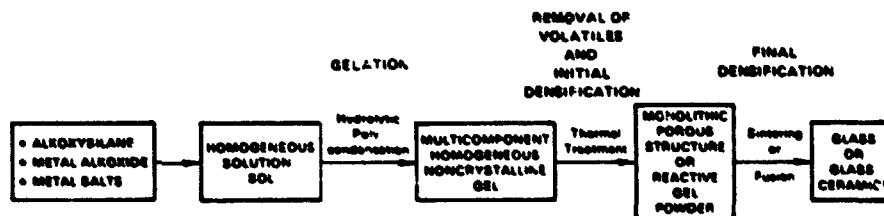
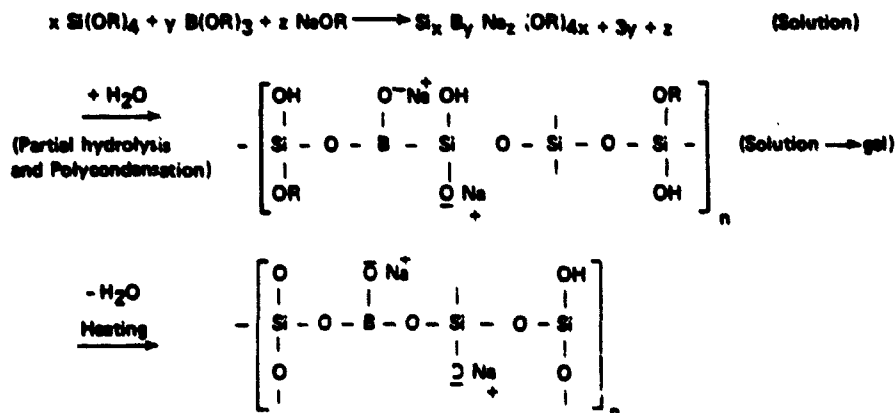


FIGURE 2. SOL-GEL PROCESS FOR GLASS MAKING--SECOND METHOD

An overall reaction of the formation of gel in a multicomponent system may be represented as follows (R is the alkyl group):



The gelling process is controlled by the following main factors: chemical nature of alkoxides and other reactants, ratio of water to alkoxides, pH of the medium and the presence of a catalyst, temperature, concentration of the reactants, and nature of solvents. The morphology (pore diameter and pore volume) as well as the structures of gel powders and gel monoliths are strongly influenced by the

gel preparation procedure.

The role of pH and the ratio of water to alkoxides are extremely important in controlling the hydrolysis and polycondensation rates. The physicochemical nature of the gel is controlled by that of the intermediates which form during the hydrolytic polycondensation reactions of alkoxysilanes and metal alkoxides. Moreover, a knowledge of the catalytic or inhibitive actions of acid or bases and other compounds is required for better control of the process. The role of pH and the ratio of water to alkoxides have been investigated by Yoldas<sup>(19)</sup>, Yamane<sup>(10)</sup>, and Sakka and Kamiya<sup>(20)</sup> primarily in single component systems, such as aluminum alkoxides,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , and  $\text{Si}(\text{OCH}_3)_4$ . The results show that the morphology, the composition of the gel, and the densification rate are strongly influenced by the pH and the ratio of water to alkoxide.

Differences in properties of gels prepared by different procedures may be attributed to the kinetics of the polymerization reactions that take place under different experimental conditions. For the alkoxysilanes, the mechanism and the rates of hydrolysis and polycondensation are different in different pH regions. In acid solutions, the rate of hydrolysis is proportional to the concentration of acid, ethoxysilane, and water. In basic solutions, the rate is proportional to the concentration of base and ethoxysilane. In strongly acid solutions, the hydrolysis reaction is rapid, the gelation tendency is low; whereas in alkaline medium, the condensation of  $\text{SiOH}$  groups take place more rapidly. The hydrolysis rate decreases sharply with increasing molecular size of the alkyl groups<sup>(14,21)</sup>.

It may be anticipated that for preparing gel monoliths, a rapid hydrolysis and polycondensation is undesirable because they will lead to rapid growth of polymer, and will trap  $\text{Si-OH}$  or  $\text{Si-OR}$  groups within the interior of large, three-dimensional molecules where they would not further condense because of steric hindrance.

The picture becomes more complex in a multicomponent system because the hydrolysis rate of metal alkoxides  $\text{M}(\text{OR})_x$ , where M is Al, Ti, Zr, etc., is much higher than that for alkoxysilanes. In a multicomponent system, the water addition sequence should also be considered in terms of the sensitivity of the different alkoxides to hydrolysis.

Some preparation procedures involving large excess of water should be considered in terms of a two-solvent colloid system where almost completely hydrolyzed polymeric species having reduced chemical reactivity are produced. Moreover, in the presence of excess water, some  $\text{M-O}$  bonds and  $\text{M-C-Si}$  bonds that are highly susceptible to hydrolysis and ionic reactions may undergo hydrolysis and reaction, and inhomogeneity might develop due to the segregation of phases in two solvents.

#### CONVERSION OF GEL TO GLASS

Gel can be converted to glass in several ways: (a) conversion of gel particulate or cast monoliths to "glass" at temperatures below  $T_g$ , (b) conversion of gel particulates to glass or glass-ceramics by sintering (with or without pressure) at temperatures above  $T_g$ , but well below melting temperatures, (c) conversion of gel particulates to glass by fusion.

The first conversion route is based on the chemical polymerization process at low temperatures. An initial major shrinkage of the cast sol/solution occurs at temperatures below 100 C due to polycondensation and subsequent contraction of the gel network. Two pieces of glass-like gel-monoliths prepared by the present author<sup>(22)</sup>, in alkaliborosilicate system, are shown in Figure 3. The difference in transparency is due to the difference in the gel preparation procedure.

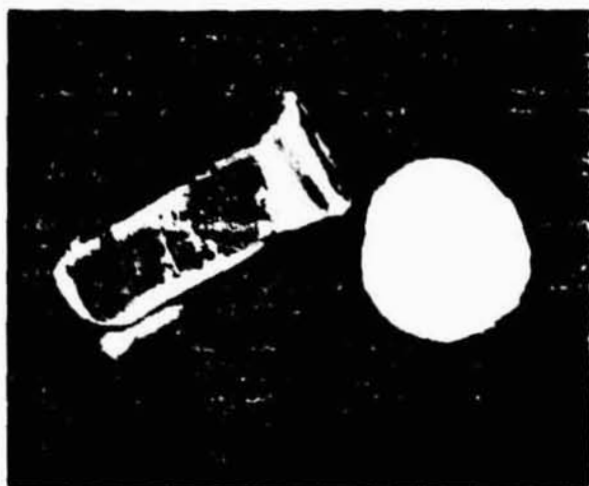


FIGURE 3. GEL MONOLITHS DRIED BELOW 100 C IN ALKALI-BOROSILICATE SYSTEM

The conversion of gel monoliths to silica glass below  $T_g$  has been investigated by several workers. Sakka and Kamiya<sup>(20)</sup> reported that the gel to glass transition starts above 800 C and the complete densification takes place at  $>1000$  C. Yamane, et al<sup>(10)</sup> studied the densification of silica gels prepared by two procedures. The densification rate and the organics removal were not the same in both cases. The final densification took place at 1070 C. Recently, Brinker and Mukherjee<sup>(23)</sup> produced gels in a multicomponent system ( $SiO_2$ ,  $B_2O_3$ ,  $Al_2O_3$ ,  $Na_2O$ ,  $BaO$ ) by two different procedures and investigated the gel-to-glass conversion. The densification rate, and the removal of organic groups were dependent on the gel preparation procedures.

Hence, the densification rate, and the final densification temperatures are significantly influenced by the morphology, composition, and chemical reactivity of the gel. These properties are controlled by the preparation procedures.

The synthesis of glasses and glass-ceramics by hot pressing gels has been reported by Dislich<sup>(5)</sup>, McCarthy, et al<sup>(24)</sup>, and by Decottignies, et al<sup>(25,26)</sup> who also reported that the sintering process during hot pressing follows the densification model based on viscous flow. The structure of the gel evolves progressively toward that of glass with loss of water and porosity.

Gel particulates, after the removal of organics and water, can be fused to glass either by conventional melting or by using concentrated heat. Concentrated heat is detrimental to making homogeneous glass from conventional glass batch because of the difficulty of attaining homogeneity, whereas a homogeneous glass can be obtained by melting multicomponent gels by concentrated heat. Mukherjee, Zarzycki, and Traverse<sup>(3)</sup> demonstrated this concept by melting gels in a solar furnace.



## MICROSTRUCTURES AND STRUCTURES OF GELS AND GEL-DERIVED GLASSES

Mukherjee, Zarzycki, and Traverse<sup>(3)</sup> reported that the microstructure of phase separated glass prepared from oxide mixtures differs from that of gel-derived glass in terms of uniformity and distribution of particle sizes. They observed that the rates of nucleation and crystallization of glasses made from the gels were much higher than those made from the mixture of oxides and concluded that the uniform cation distribution, gel structure, and the residual hydroxyl groups contribute to these properties.

Weinberg and Neilson<sup>(13)</sup> observed that the miscibility temperature of a glass composition in the sodium silicate system is elevated when the glass is prepared via the gel route. They attributed the origin of this effect to the enhanced water content in the gel-derived glass. Work of Mukherjee and Zarzycki<sup>(8)</sup> indicates that the microstructure as well as the thermal history of the gel also contribute to the structure and microstructure of the glasses. They observed that the gel prepared from the gelation of silica sol (Method I) crystallized faster than that prepared by the polymerization of alkoxysilane (Method II). The gel made by the polymerization of alkoxysilane is a glass-like noncrystalline solid with a much higher resistance to crystallization. When thermally aged (~500 C), a noncrystalline submicron size  $La^{+}$ -rich phase (20 Å size) dispersed in the silica network is developed. Phalippou, Zarzycki and Lalane<sup>(27)</sup> determined apparent activation energy of crystallization of pure silica gel prepared by two methods. The apparent energy of activation for crystallization of gel prepared by Method II is much higher than that of gel prepared by Method I.

Recently, the author<sup>(28)</sup> has studied the preparation of gels in alkali-borosilicate systems by different procedures based on the polymerization of alkoxysilane (Method II). The infrared spectra of the gels, prepared by two different procedures are shown in Figure 4. The first procedure consists of the following steps: (i) mixing tetraethyl orthosilicate with anhydrous ethanol, (ii) adding boric acid dissolved in methanol, (iii) adding sodium methylate, (iv) initiating gelation by adding less than the theoretical water required for the complete hydrolysis. The second procedure consists of the following steps: (i) mixing tetraethyl orthosilicate with anhydrous ethanol, (ii) deliberate initial partial hydrolysis of ethyl silicate in the presence of an acid catalyst, (iii) adding trimethyl borate, (iv) further partial hydrolysis of alkoxides, (v) adding an aqueous solution of sodium acetate.

It is evident from the figure that the position and the features of the absorption band (resulting from Si-O bond stretching) are not the same in both the gels. The peak position of the gel prepared by the first procedure is at  $1000\text{ cm}^{-1}$  whereas the peak position obtained with gel prepared by the second procedure is at  $1060\text{ cm}^{-1}$ . The peak position did not shift by any thermal treatment steps (up to 500 C). The humidity treatment which had an effect on both the hydrolysis and the removal of chemically bonded alkoxy groups did not shift the peak position.

In vitreous silica, the absorption band resulting from Si-O bond stretching is at  $1100\text{ cm}^{-1}$ . The Si-O stretching vibration of polysiloxanes containing Si-O linkage gives rise to the absorption band in the region of  $1010\text{ cm}^{-1}$  to  $1090\text{ cm}^{-1}$ . The position of the peak depends on the nature of the polymers. There are some differences between cyclic and open-chain compounds. For the cyclic compounds, the position of absorption peak shifts with increased ring size. In trimer compounds, the band appears at  $1018\text{ cm}^{-1}$  while in the higher ring, it falls in the range of  $1076$  to  $1056\text{ cm}^{-1}$ <sup>(29)</sup>. Most likely, the differences in the peak positions are due to the structural differences in the polymer, the nature of which is controlled by the gel preparation procedure.

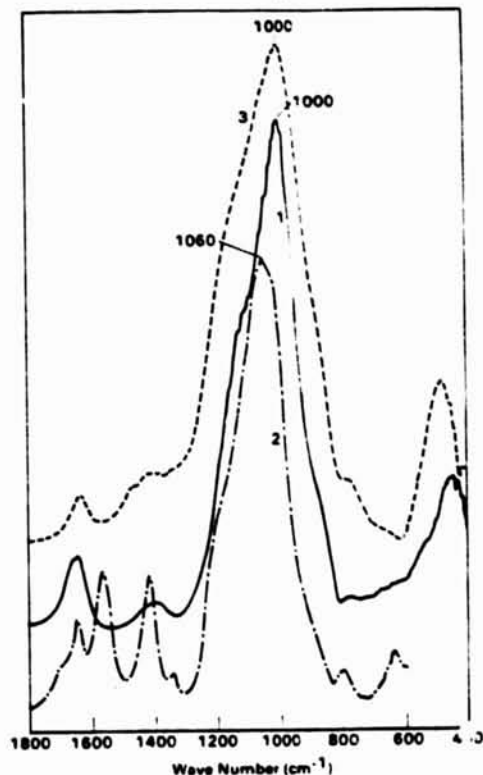


FIGURE 4. INFRARED SPECTRA OF GELS  
(NO. 1)--PROCEDURE 1  
(NO. 2)--PROCEDURE 2  
(NO. 3)--PROCEDURE 1 AFTER THERMAL  
TREATMENT UP TO 500 C

It is extremely difficult to introduce Ti ions into the silicate network as Si-O-Ti (fourfold coordination), Ti ions separate in the form of droplets of  $\text{TiO}_2$  (sixfold coordination) which crystallizes and increases the thermal expansion coefficient. The low or zero thermal expansion coefficient of the glasses in the  $\text{SiO}_2$ - $\text{TiO}_2$  system is attributed to the fourfold coordination of  $\text{Ti}^{4+}$  ions (30). Mukherjee (31) prepared gels in the  $\text{TiO}_2$ - $\text{SiO}_2$  system of different compositions (up to 50 wt%  $\text{TiO}_2$ ) by two different procedures, based on the polymerization of tetraethoxy silane with titanium n-butoxide. In the first procedure, the polycondensation was effected by exposing the solution to atmospheric moisture without deliberate addition of water. In the second procedure, the gelation was done rapidly by adding ammoniacal water. The physical nature and microstructure of the gels were markedly different. In the first procedure, transparent glass-like gel was obtained, where in the second procedure a white powdery gel was obtained. The microstructures of the gels are shown in Figure 5. The gels after drying at 100 C were examined by X-ray diffraction. No crystallinity was observed with any composition (up to 50 wt%  $\text{TiO}_2$ ).

The infrared spectra of gels prepared by two procedures are shown in Figure 6. The presence of absorption band at  $960\text{-cm}^{-1}$  indicates that Ti ions are in the fourfold coordination state (32). Note that the half width of the absorption band of the gel prepared by the second procedure is much smaller than that of the gel prepared by the first procedure. This may be due to the change in the molecular structure.



(a)



(b)

FIGURE 5. ELECTRON MICROGRAPHS OF  
GELS IN THE  $\text{TiO}_2$ - $\text{SiO}_2$  SYSTEM:  
(a) PROCEDURE 1,  $\text{TiO}_2$ , 10%  
(b) PROCEDURE 2,  $\text{TiO}_2$ , 10%

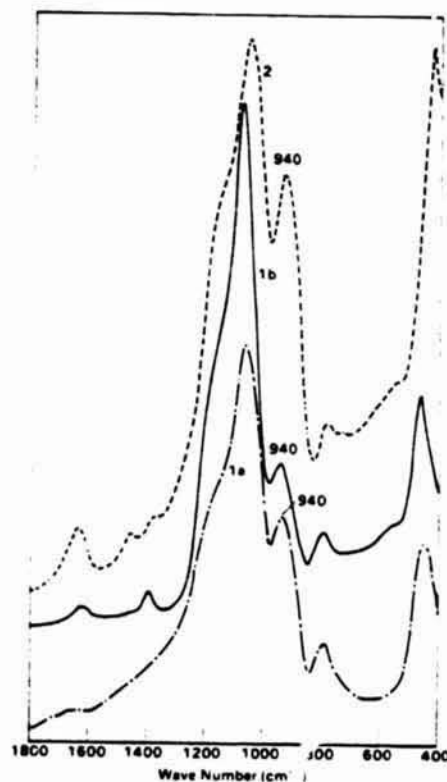


FIGURE 6. INFRARED SPECTRA OF GELS  
IN THE  $\text{TiO}_2$ - $\text{SiO}_2$  SYSTEM.  
(1a)--PROCEDURE 1  
(1b)--PROCEDURE 2,  $\text{TiO}_2$ , 10%  
(2) --PROCEDURE 1,  $\text{TiO}_2$ , 25%

Hence, it is evident that the sol-gel process leads to the preparation of glasses which are hard to prepare because it is extremely difficult to introduce certain cations into the silicate network as glass formers by the melting process.

#### ADVANTAGES

Several advantages are associated with the preparation of glasses via the gel route. They may be summarized as follows: (a) particulate as well as monolithic glass-like transparent materials can be formed without melting; (b) distribution of cations are in a molecular scale, unique and uniform microstructures can be obtained in the liquid-liquid immiscibility zone; (c) incorporation of certain cations in a particular coordination state can be achieved; (d) suitable for making ultrapure glasses because many alkoxides are liquids which can be purified by distillation; (e) highly flexible for depositing "glass" coatings at low temperatures; (f) both the macroscopic homogeneity and submicroscopic homogeneity of glass prepared by the sol-gel process are considerably better; and (g) homogeneous glass can be obtained at lower melting temperatures and in shorter melting times<sup>(3)</sup>.

#### APPLICATIONS

Present commercial applications of the sol-gel process, except the coatings on glass, are somewhat rare. However, various applications that are of potential importance are as follows: (a) monolithic glass blocks without melting, (b) coatings: optical, protective, dielectric, antireflective, at low temperatures, (c) high-temperature and high-strength glass and glass-ceramic fibers, (d) starting materials for making highly homogeneous ultrapure glasses (e.g., optical glass, laser glass, glass for optical communications), (e) high-temperature glasses containing components that volatilize at high temperatures, (f) high-temperature glass frits at low temperatures, (g) homogeneous, ultrapure, multi-component batch for glass processing in space, (h) hollow shells for laser fusion targets, (i) insulating glass or glass-ceramics foams/fibers, (j) bonding agents for refractory materials, and (k) low expansion glass.

#### ACKNOWLEDGEMENTS

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# GELS AND GEL-DERIVED GLASSES IN THE $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ SYSTEM

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## ABSTRACT

The containerless melting of high-purity multicomponent homogeneous gels and gel-monoliths offers a unique approach to making ultrapure multicomponent optical glasses in the reduced gravity environment of space. Procedures for preparing and characterizing gels and gel-derived glasses in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system are described. Preparation is based on the polymerization reactions of alkoxysilane with trimethyl borate or boric acid and a suitable sodium compound. The chemistry of the gelling process is discussed in terms of process parameters and the gel compositions. The physicochemical nature of gels prepared by three different procedures were found to be significantly different. Infrared absorption spectra indicate finite differences in the molecular structures of the different gels. The melting of the gel powders and the transformation of porous gel-monoliths to transparent "glass" without melting are described.

## INTRODUCTION

The possibility of containerless melting of glass in the reduced gravity environment of space will open a unique approach to preparing ultrapure glass or melts free from contamination from containers. Consequently, the optical and electrical properties of the melt which are strongly influenced by trace impurities can be of superior quality. However, because of the absence of gravity-induced convection currents, homogenizing glass during melting of conventional raw materials will be difficult in the space environment. Homogeneous, glass-like, gels and gel-monoliths prepared by the polymerization reaction of alkoxysilane with other metal alkoxides and/or with suitable metal salts<sup>[1-7]</sup> can be used as the batch materials for the containerless melting of glasses in the reduced gravity environment in space. This approach could lead to a process for the preparation of ultrapure optical glasses.

In the present work, three procedures for the preparation of gels in the multicomponent  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system are investigated. The physicochemical nature of gels and gel-derived glasses has been characterized. Attempts are made to understand the physicochemical properties of the gels in relation to the chemistry of the gelling process. The transformation of different gels and gel-monoliths to glasses by melting and by densifying monolithic gels are investigated.

## EXPERIMENTAL WORK AND RESULTS

### Compositions

The starting batch composition of the glasses investigated are given in Table I. The glass transition temperatures of the same compositions prepared by the melting conventional batches are 520 C and 600 C for Composition 1 and

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Composition 2, respectively. Composition 1 having high  $\text{Na}_2\text{O}$  content lies away from the metastable liquid-liquid immiscibility zone.

Composition 2 lies inside the metastable liquid-liquid immiscibility zone and was chosen for investigating the liquid-liquid phase-separation behavior of gel-derived glasses which is discussed elsewhere [8].

TABLE I  
Compositions of Gels

Composition	Weight percent			Mol percent		
	$\text{SiO}_2$	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{SiO}_2$	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$
1	60	15	25	61.78	13.30	24.91
2	84	12	4	85.53	10.52	3.95

#### Gel preparation procedures

The following starting chemicals were used as sources of different oxides: tetraethoxysilane (liquid), methanolic solution of boric acid, trimethyl borate (liquid), methanolic solution of sodium methoxide, aqueous solution of sodium nitrate, and aqueous solution of sodium acetate. Three procedures using three sources of  $\text{Na}_2\text{O}$  were developed and investigated. Gels of Composition 1 in particulate forms were prepared by all three procedures. Gels of Composition 2 were prepared by Procedure I and III in particulate and in monolithic forms.

**Procedure I.** The starting compounds were tetraethoxysilane, boric acid, and sodium methoxide. Gels were synthesized in nonaqueous solvents. The general procedure consisted of the following steps:

(i) Mixing tetraethoxysilane with three times its volume of anhydrous ethanol at 40 C

(ii) Partial hydrolysis of tetraethoxysilane (a) by exposing the solution containing acid catalyst ( $\text{HCl}$ ) to the ambient atmosphere and stirring at 40 C for about 1 hour or (b) by adding a small proportion of water acidified with  $\text{HCl}$  and stirring for 10 to 15 minutes at 40 C. The proportion of water that could be added was in the range 0.1 to 0.2 mol per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The concentration of  $\text{HCl}$  was in the range .002 to .0004 mol per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ .

(iii) Adding  $\text{H}_3\text{BO}_3$  dissolved in hot anhydrous methanol (30 g/100 ml) and stirring at 40 C for 2 hours resulted in a solution pH 4 to 6.

(iv) Adding methanolic solution of sodium methoxide, a transparent solution is produced if the proportion of acidified water added during partial hydrolysis was sufficiently low. The final solution was in the pH range 9 to 10. The solution was stirred for 2 to 3 hours at room temperature.

(v) The final solution was diluted with anhydrous ethanol to a concentration about 40 g metal oxide per liter and was left exposed to the ambient atmosphere for gelation.

The gelling time of the solution decreased (a) with increased  $\text{Na}_2\text{O}$  concentration, (b) with increased metal oxide concentration, (c) with increased proportion of water and acid added during the initial hydrolysis, (d) with increased humidity of the ambient atmosphere during the final gelling stage.

The gelling time of the solution (40 g/liter) of Composition 1 was in the range 1 to 3 hours, whereas the gelling time of the solution of same concentration of Composition 2 was about 16 hours.



To prepare gel-monoliths of Composition 2, the final solution after dilution with anhydrous ethanol was poured into a glass or preferably plastic container and allowed to form gel in the ambient atmosphere. Transparent gel-monoliths thus were dried under carefully controlled conditions at room temperature.

**Procedure II.** The starting compounds were tetraethoxysilane, boric acid, and sodium nitrate. Sodium nitrate, being insoluble in alcohols, was added as a very dilute aqueous solution at the final stage of the reaction. The general procedure consisted of the following steps:

- (i) Mixing tetraethoxysilane with three times its volume of anhydrous ethanol at 40 C
- (ii) Partial hydrolysis of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  with acidified water at 40 C for about 1 hour. The proportion of water was around 0.5 mol per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and the HCl acid concentration was in the range 0.0004 to 0.0006 mol per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The solution pH was in the range 3 to 4.
- (iii) Adding methanolic boric acid and stirring for about 1 hour at 40 C
- (iv) Adding aqueous sodium nitrate solution to the mixture and stirring for about 3 hours. The amount of water added with sodium nitrate was sufficiently high so that no precipitation of sodium nitrate occurred after mixing with the alcoholic reaction mixture. The pH of the final solution was around 3.5. The total amount of water at this stage was around 20 mols per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ .

The concentration of the solution was approximately 70 g metal oxide per liter. The gelation occurred as solution was maintained at 40 C for 2 to 3 days.

The gelling time decreased with increased pH of the final solution which was controlled by the concentration of acid added during initial hydrolysis and by the concentration of the final solution after the addition of  $\text{NaNO}_3$  solution. The pH can also be increased by adding a weak base at the final stage.

**Procedure III.** The starting compounds were tetraethoxysilane, trimethyl borate, and sodium acetate. An aqueous solution of sodium acetate was added at the final stage of the reaction. The general procedure consisted of the following steps:

- (i) Mixing tetraethoxysilane with three times its volume of anhydrous ethanol at 40 C for 10 minutes
- (ii) Partial hydrolysis with acidified water at 40 C for about 30 minutes. The proportion of water was 1 mol per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The concentration of acid was 0.02 mol per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The solution pH was around 0.2.
- (iii) Adding trimethyl borate and stirring for about 3 hours
- (iv) Adding an aqueous solution of sodium acetate acidified with acetic acid. The solution was stirred and was left for gelation. The total water in the final solution was related to the  $\text{H}_2\text{O}$  content of the composition and the concentration of sodium acetate solution. The total amount of water for Composition 1 was in the range 30 to 60 mols per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , whereas the total amount of water for Composition 2 was as low as 1.6 mols per mol of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ . The final solution pH was in the range 4 to 5. The gelling time decreased (a) with increased  $\text{H}_2\text{O}$  concentration, (b) with increased concentration of sodium acetate solution, (c) with decreased acidity of the solution before the addition of sodium acetate. The gelling time of the solution (40 g metal oxide per liter) of Composition 1 was 30 to 60 minutes. That for solutions of same concentrations of Composition 2 was 5 to 12 hours.

The gel-monoliths of Composition 2 were prepared by pouring the final solution into a closed container which was left for gelation. Gel-monoliths were dried carefully to avoid cracking.

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#### Thermal treatment and characterization of gels

Thermal treatment procedures for the removal of organics and volatiles consisted of heating in steps at a low rate (10 C/hour) up to 500 C. The first soaking temperature after initial drying at 60 C for about 2 days was 150 C to remove adsorbed water and solvents. The second soaking temperature was 350 C where combustion of the organic groups occurs. An endothermic peak at around 150 C and an exothermic peak at around 350 C obtained with the DTA curves indicate these phenomena. The organics removal rate can be increased by taking further steps such as the thermal treatment of gels in a humidity chamber at around 70 C, or an oxygen atmosphere during the thermal treatment.

The removal rate is related to the gel preparation procedure as well as the gel composition. The results suggest that different organic removal rates from gels prepared from the same composition but by different procedures could be related to (1) the chemical nature of the residual organics (2) the nature and size of pores in the gels, and (3) the rate of pore closure at temperatures below 500 C.

The surface areas of the gel particles and gel-monoliths were measured by argon adsorption using a Micrometrics instrument (Model 2205). The surface areas of Composition 1 gel particles were measured through a range of temperatures holding in the instrument at each for 1/2 hour before the measurement. The surface areas of gel-monoliths of Composition 2 were measured after thermal treatment at different temperatures in a furnace in air. The results are shown in Table II. It is evident from the results that the surface areas are strongly influenced by the preparation procedures and by the thermal treatment.

TABLE II  
Surface areas of gels and gel-monoliths

Gel preparation procedure	Composition	Thermal treatment		Surface area (m <sup>2</sup> /gm)
		Holding time (hr)	Holding temp. (C)	
<u>Gel particulates</u>				
I	1	1/2	150	40
I	1	1/2	300	42
I	1	1/2	500	0
III	1	1/2	300	25
III	1	1/2	400	100
III	1	1/2	500	11
<u>Gel-monoliths</u>				
I	2	96	150	381
I	2	4	350	301
I	2	4	500	253
I	2	1/4	750	3
III	2	4	500	442

X-ray diffraction powder patterns of gels of Composition 1 were taken after thermal treatment at different temperatures up to 600 C. The results

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the gels prepared by Procedure I and Procedure III were noncrystalline and that no crystallinity developed on thermal treatment at temperatures up to 600 C. The maximum thermal treatment at 600 C was 40 hours. The gels prepared by Procedure II were crystalline due to the presence of  $\text{KNO}_3$ . However, the crystallinity decreased with increased thermal treatment time at 500 to 600 C.

Gel-monoliths of Composition 1 prepared by Procedure I and Procedure III were noncrystalline after thermal treatments at temperatures  $\leq 500$  C. Maximum heat treatment at 500 C was 4 hours. Crystallinity developed after heat treatment at temperatures above 600 C during the gel-to-glass transformation stage.

#### Conversion of gels to glass

Melting of gels. The gels of Composition 1 after the thermal treatment at 500 C were melted at temperatures at and above 1000 C to obtain clear glass after eliminating residual carbons. Carbon retention in the gels depended on the gel preparation procedure and thermal treatment. Subsequent elimination of carbon from the glass was a function of time, temperature, and ambient atmosphere (i.e., oxygen potential) of melting. Time and temperature required for obtaining visually colorless and transparent glasses of Composition 1 are given in Table III. It is evident that residual carbon was eliminated most rapidly from Procedure II gels and most sluggishly from Procedure III gels.

TABLE III

Effect of time and temperature on carbon removal during the melting of gels of Composition 1

Gel preparation procedure	Melting temperatures (C)	Melting time (hr)	Appearance
I	1000	2	Transparent, grey colors
I	1000	3	Transparent, colorless
I	1100	2	Transparent, colorless
I	1200	1	Transparent, colorless
II	1000	1	Transparent, colorless
III	1000	1	Transparent, grey to black
III	1000	4	More transparent, greyish
III	1200	2	Transparent, nearly colorless
III	1200	4	Transparent, colorless

Densification of gel-monoliths. Porous gel-monoliths of Composition 2 prepared by Procedure I were heat treated at different temperatures after the removal of organics at 500 C. The samples were examined and x-ray diffraction patterns were taken to detect the crystallinity developed. The results of the experiments are shown in Table IV. The physical appearance of a glass-like gel-monolith obtained after densification at 700 C for 1/2 hour is shown in Figure 1 (page 10).

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TABLE IV  
Thermal treatments for the porous gel monoliths of composition 2

Gel preparation procedure	Sample	Thermal history		Heat treatment		Physical appearance	Crystallinity
		(C)	(hr)	(C)	(hr)		
I	(1)	150 350	72 1-1/4	500	4	Transparent, porous	Noncrystalline
I	(2)	150 350 500	72 1-1/4 4	600	1/4	Transparent, open porosity exists	Noncrystalline
I	(3)	150 350 500	72 1-1/4 4	600	1/2	Transparent, open porosity exists	Noncrystalline
I	(4)	150 350 500	72 1-1/4 4	650	1/4	Transparent and densified	Noncrystalline
I	(5)	150 350 500	72 1-1/4 4	650	1/2	Transparent and densified	Noncrystalline
I	(6)	150 350 500	72 1-1/4 4	700	1/2	Transparent and densified (see Fig. 1)	Noncrystalline
I	(7)	150 350 500	72 1-1/4 4	750	1/2	Transparent and densified	Crystallinity detected $\beta$ -quartz
I	(8)	150 350 500	72 1-1/4 4	750	2	Completely white and opaque	Crystalline, $\alpha$ -cristobalite
I	(9)	150 350 500	72 1-1/4 4	800	1/4	Completely white and opaque	$\alpha$ -cristobalite
I	(10)	150 350 500	72 1-1/4 4	850	1/4	Completely white and opaque	$\alpha$ -cristobalite
III	(11)	Slowly heated to 500 C		500 C	4	Transparent, porous	Noncrystalline
III	(12)	Slowly heated to 500 C		700	1/2	Transparent with slight opacity	Crystallinity detected, $\beta$ -quartz

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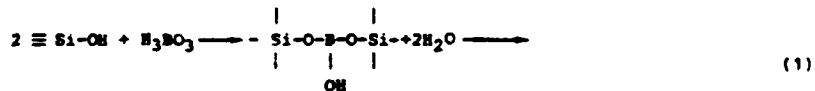
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## DISCUSSION

The formation of the condensed polysilicates and subsequent gelation of tetraethoxysilane is the result of a complex sequence of hydrolysis and condensation reactions. The complexity increases in a system with components having different reactivity and solubility. Gelling is controlled by the process parameters such as chemical nature of alkoxides and other reactants, molecular ratio of water to alkoxides, the presence of catalysts and pH of the medium, temperature, concentration of reactants, and nature of solvents.<sup>[6]</sup>

In this multicomponent system having reactants of markedly different chemical nature, it is extremely difficult to change the process parameters independently of each other. Moreover, the addition of aqueous solution such as sodium nitrate and sodium acetate which are insoluble in alcohol should be considered in the context of the liquid-liquid immiscibility<sup>[9]</sup> existing in the  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and  $\text{H}_2\text{O}$  system. The possibility of segregating water-soluble phases under certain experimental conditions should be investigated. To homogeneously incorporate a high proportion of  $\text{Na}^+$  ions (which is not a network former) into a gel structure is complex and difficult.

In Procedure I, all reactants are soluble in alcohols and it is presumed that a homogeneous solution of the molecular species was obtained at the final stage. However, the sequence of reactions may be postulated as follows: In acid medium, the hydronium ion attacks the polar  $\equiv\text{Si}-\text{OC}_2\text{H}_5$  bond and forms  $\equiv\text{Si}-\text{OH}$  groups<sup>[10]</sup>. However, in this type of nucleophilic displacement reactions the reactivity decreases as more groups on the silicon atom are displaced. The polysilicate is formed through condensation of silanol groups:  $\text{SiOH}$ ; or silanol and alkoxy groups  $(\equiv\text{Si}-\text{OC}_2\text{H}_5)_4$ . The further attack of  $\equiv\text{Si}-\text{OC}_2\text{H}_5$  bond in the polysiloxane by  $\text{H}_2\text{O}$  might also be hindered by the steric effect of ethoxy groups. Thus, hydrolysis of ethylsilicate is controlled by the electronic and steric effects developed during hydrolysis. Hence under mild conditions of hydrolysis at room temperatures and with a small proportion of  $\text{H}_2\text{O}$ , the formation of low-molecular-weight molecules takes place. Recent work of Peace, et al<sup>[11]</sup> on the hydrolysis of alkoxy silanes suggests that the polymers at the initial stage of hydrolysis might have ring structure—perhaps a dimer with two connected rings each containing four silicon atoms. Boric acid itself or methyl borate  $\text{B}(\text{OCH}_3)_3$  which could form by the reaction of methanol with boric acid<sup>[12]</sup>, can react with silanol or alkoxy groups and form  $\equiv\text{Si}-\text{O}-\text{B}$  bonds in the following way:<sup>[9]</sup>



An advantage of the addition of boric acid is that certain amount of water is liberated during the reaction of  $\text{H}_3\text{BO}_3$  either with silanol groups or with alcohols and this water produced in situ could effectively induce further hydrolysis without addition of free  $\text{H}_2\text{O}$ . After subsequent addition of sodium methoxide solution, the pH of the solution increases above 9, and consequently the mechanism and kinetics of hydrolysis and polycondensation changes.<sup>[10]</sup> Moreover, sodium methoxide being highly susceptible to hydrolysis (e.g.,  $\text{NaOCH}_3 + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{CH}_3\text{OH}$ ) produces  $\text{OH}^-$  groups which

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enhance the polycondensation and growth of the polymeric particles.<sup>[10]</sup> Subsequently, the solution absorbs sufficient water from the atmosphere or when free water is added, the gelation occurs rapidly. The observed increased gelling rate with increased proportion of water at the initial stage of hydrolysis suggest that any free water remaining before adding sodium methoxide cause the generation of hydroxyl ions which enhance the gelation. The decreased gelling time with increased  $\text{NaOCH}_3$  and with increased humidity also indicates the hydrolytic reaction of the  $\text{NaOCH}_3$  and the catalytic activity of  $\text{OH}^-$  groups. The incorporation of  $\text{Na}^+$  ions into the gel structures might take place as follows:  $\text{NaOH}$  generated by the hydrolysis of  $\text{NaOCH}_3$  might react with  $\equiv \text{Si}-\text{OC}_2\text{H}_5$  group to produce  $\equiv \text{SiONa}$ <sup>[9]</sup>. Sodium methoxide having strong ionic character might undergo ion exchange with  $\text{H}^+$  ion of silanol groups at high pH and may produce  $\equiv \text{SiONa}$ . A secondary reaction forming tetra-coordinated boron of the type  $\text{Na}[\text{B}(\text{OCH}_3)_4]$  might take place when free or partially hydrolyzed  $\text{B}(\text{OCH}_3)_3$  reacts with  $\text{NaOCH}_3$ <sup>[13]</sup>.

In Procedure II, the initial reactions of tetraethoxysilane with boric acid are anticipated to be similar to those described for Procedure I. However, the addition of higher proportion of water and of acids would lead to more complete hydrolysis of ethoxysilane. The polymer molecules contain less unreacted ethoxy groups, and the solution shows little tendency to gelation. Sodium nitrate additions, unlike  $\text{NaOCH}_3$  or sodium acetate, do not increase the pH. Consequently, the gelling time is long. Sodium nitrate, being not reactive to other reactants and being insoluble in alcohols, segregates in the aqueous phase and precipitates as  $\text{NaNO}_3$  as the gels dry, as evidenced by the x-ray diffraction results. The heat treatment at 500 C or above decomposes the nitrate and reactive  $\text{Na}_2\text{O}$  forms thus, the crystallinity decreases with the heat treatment. However, excess water and the low gelation rate are beneficial for hydrolyzing alkoxy groups and subsequent removal of organics.

In Procedure III, the initial stage of the hydrolytic reactions in presence of high proportion of water and acid is similar to that of Procedure II. Consequently, the hydrolysis is more complete and the solution being at low pH (2) shows less tendency to form gels. When sodium acetate solution is added, the gelation occurs due to introducing high concentration of  $\text{OH}^-$  ions present in sodium acetate solution; the pH of the solution increases to higher gelling rate region<sup>[10]</sup> and gelation occurs rapidly. The surface areas of gels produced from the low pH solution is large because, in strongly acid medium, the polymeric particles cannot grow<sup>[14]</sup>, consequently gels produced from submicron particles have higher surface areas.

The significant difference in the surface areas of the gels prepared by the different procedures (Table IV) can be interpreted in terms of the effect of pH on the size of the particles. When the gelation is done with solution of low pH (2) the particle sizes are smaller, consequently, the pore sizes are finer. The incorporation of  $\text{Na}^+$  ions into the gel structure might occur either by the reaction of  $\text{NaOH}$  produced by the hydrolysis of sodium acetate with  $\equiv \text{Si}-\text{OC}_2\text{H}_5$  group or by the exchange of  $\text{H}^+$  ions of the silanol groups with  $\text{Na}^+$  ions of acetate solution<sup>[15]</sup>. But, a portion of  $\text{Na}^+$  ions might remain in water phase and could produce a nonuniform distribution of  $\text{Na}^+$  ions in the gels.

The infrared absorption spectra of Composition 1 gels prepared by different procedures and after thermal treatments at different temperatures were taken by the KBr pellet technique, using Digilab FTS14 spectrophotometer and are shown in Figure 2. It is evident from the figure that the position and the features of the absorption bands resulting from Si-O bond stretching are not the same in all the gels. The peak positions were not shifted by thermal treatment steps up to 500 C or by the humidity treatment that had affected both hydrolysis and removal of chemically bonded alkoxy groups.

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The difference in the nature of the molecular structure of the gels as depicted in the infrared spectra, might have been originated due to (a) the difference in the structural incorporation of  $\text{Na}^+$  ions with the polymeric species of the gels, or (b) the difference in the molecular structures of the networks produced during the hydrolytic polycondensation process [11, 16, 17]. The effects of different thermal treatments above 500 C on the change in molecular structures of the gels have not been studied. However, the infrared and Raman spectra of glasses made from the different gels of Composition 1 indicate that the melting at higher temperatures (1100 to 1200 C) appears to be sufficient to give an equilibrium melt for each gel.

The preliminary results of the densification studies of the gel-monoliths of Composition 2 (see Table IV) shows that the porous gel-monoliths can be densified to transparent "glass" by heat treatment at temperatures above the glass-transition temperatures. The results show that the gels have a strong tendency to crystallize at higher temperatures. However, the gels of Composition 1 prepared by Procedure I and Procedure II do not crystallize on heat treatment at temperatures above  $T_g$  for a prolonged period (for example, 40 hours at 600 C). The basic reason for the crystallization of gels of Composition 2 is not understood yet. The heat treatment of gels in the  $\text{La}_2\text{O}_3$ - $\text{SiO}_2$  system shows a similar crystallizing tendency. [18] It is reported by several workers [19, 20] that the silica gels and amorphous silica powders and silica glass crystallize in presence of sodium or potassium salts in the 800 to 850 C range. It is suggested [19, 20] that adsorbed cations entered the lattice at elevated temperatures causing the Si-O-Si bridges to rupture, thereby collapsing the structure and lowering the densification temperatures. The crystallization of gels of Composition 2 is presumably due to the high reactivity of the mobile  $\text{Na}^+$  ions on the less tight gel structure and subsequent rupture of the Si-O-Si bonds. The high hydroxyl contents might also enhance crystallization. [21] The absence of crystallization tendency in Composition 1 gels may be a compositional effect. A viscous low melting alkali borosilicate glassy phase might form at lower temperatures.  $\text{Na}^+$  ions being structurally incorporated into this glassy phase becomes less reactive and mobile, consequently, the stability of the gels toward crystallization above  $T_g$  is prolonged.

#### CONCLUSIONS

Gels and gel-monoliths of different compositions in the  $\text{Na}_2\text{O}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  system can be prepared by three different procedures. The physicochemical nature of the gels prepared by the different procedure are significantly different. The chemistry of the gelling process is controlled by the various process parameters and by the composition of the gels in a particular system. Molecular structures of gels having Composition 1 (wt %)  $\text{SiO}_2$  60,  $\text{B}_2\text{O}_3$  15,  $\text{Na}_2\text{O}$  25 prepared by different processes are not identical. However, the melting of the gels at 1100 to 1200 C is sufficient to give equilibrium in the melts from the different gels. Gel-monoliths having a composition (wt %)  $\text{SiO}_2$  84,  $\text{B}_2\text{O}_3$  12,  $\text{Na}_2\text{O}$  4 can be transformed into transparent "glass" by heat treatment at temperatures above  $T_g$ . But the gel has a strong tendency to crystallize during gel-to-"glass" transformation. The rupture of Si-O-Si bonds by highly mobile  $\text{Na}^+$  ions in the less dense gel structure might be the reason for the crystallization of silica phase.

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Fig. 1. Composition 2 gel-monoliths after treatment at 700 C for 1/2 hour.

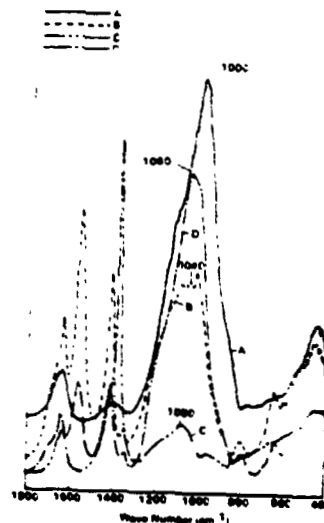


Fig. 2. Infrared spectra of air-dried gels. A. Procedure I, without deliberate addition of acidified water. B. Procedure I, initial hydrolysis with acidified water, acidified with acetic anhydride before adding  $\text{NaOCH}_3$ . C. Procedure II. D. Procedure III.

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**Crystallization Behavior of Gels and Gel-Monoliths  
in the  $\text{Na}_2\text{O}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  System**

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**Abstract.** - Gels and gel-monoliths in the sodium borosilicate system were prepared by the hydrolytic polycondensation of alkoxysilane with trimethyl borate or boric acid and a suitable sodium compound. Three different procedures using three different sources of  $\text{Na}_2\text{O}$  were developed. Crystallinity of different gel-powders and gel-monoliths of two compositions were examined after thermal treatment at different temperatures above the glass transition temperature ( $T_g$ ). Results indicate that the stability of the gels toward crystallization during gel-to-"glass" transformation around  $T_g$  depends on the composition, previous thermal history, and time and temperature of heat treatment. The results are explained in terms of gel structures and the nature and role of sodium ions in gel structures.

**1. Introduction.** - In recent years, the preparation of noncrystalline silicate gels and gel-monoliths and their subsequent conversion to glasses and glass-ceramics by sintering or by melting have been reported by several researchers [1, 2, 3, 4, 5]. Research activities and their scientific and technological importance have been critically reviewed by Mukherjee [6] and by Sakka and Kamiya [7].

The stability of the gels or gel-derived glasses toward crystallization (i.e., the kinetics of the ordering process during gel-to-glass transformation), depends on the nature of the noncrystallinity of the gel structure. The formation of a noncrystalline phase by rapidly quenching molten or evaporated solids is not unusual because the kinetic forces (e.g., the rate of quenching of melt or vapor and high viscosity of melts) play a major role in preventing the crystallization.

The key element in developing noncrystallinity may result from chemical polymerization conditions which can produce certain stable disordered polymeric molecular configurations. Kinetic factors such as the cooling rate or viscosity do not appear to be the major force in the formation of inorganic gels from solutions. Hence, the kinetics of the ordering process for the gels and gel-derived glasses appears to be different from those of the vitreous solids produced from the melts [3, 8, 9, 10, 11, 12]. The effects of minor components and impurities on the kinetics of crystallization of gels are also found to be different from those observed with the glasses obtained by the fusion of molten oxides [9, 13, 14, 15, 16].

The objectives of the present work were to (a) prepare gels and gel-monoliths in the  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system by different gel preparation procedures; (b) investigate the stability of the gels toward crystallization during gel-to-glass conversion at temperatures around  $T_g$  and (c) investigate the effects of chemical leaching of sodium ions from the porous gels on the crystallization rate during gel-to-glass conversion.

2. Experimental Work and Results. - The batch compositions of the gels investigated are given in Table 1. The  $T_g$  of the glasses of the same compositions prepared by melting conventional batches are 520 C for Composition 1 and 600 C for Composition 2.

Table 1: Composition of Gels.

Composition	Weight Percent			Mol Percent		
	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O
1	60	15	25	61.78	13.30	24.91
2	84	12	4	85.53	10.52	3.95

3. Gel Preparation Procedures. Three procedures using three sources of Na<sub>2</sub>O were developed and investigated. Gels of Composition 1 were prepared in particulate forms. Gels of Composition 2 were prepared in particulate and in monolithic forms. Starting chemicals for each procedure are given in Table 2. Each procedure followed a five step routine: mix silicon compound with ethanol, partial hydrolysis with acidified H<sub>2</sub>O, add boron compound, adjust pH, and gelation. See Reference 16 for procedural details.

Table 2: Starting Chemicals for Gel Preparation.

Procedure I	Procedure II	Procedure III
Si(OR) <sub>4</sub> (liquid) where R = C <sub>2</sub> H <sub>5</sub> , CH <sub>3</sub>	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> (liquid)	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> (liquid)
H <sub>3</sub> BO <sub>3</sub> in methanol	H <sub>3</sub> BO <sub>3</sub> in methanol	B(OCH <sub>3</sub> ) <sub>3</sub> (liquid)
NaOCH <sub>3</sub> in methanol	NaNO <sub>3</sub> in excess water	Sodium acetate in water
Solvent: Ethanol	Solvent: Water and ethanol	Solvent: Water and ethanol

Thermal history and heat treatment for Composition 1 gels and Composition 2 gel-monoliths are indicated in Table 3. Crystallization was monitored by the differential thermal analysis (DTA) and X-ray powder diffraction techniques. Experimental results are shown in Table 3. All gels prepared by Procedures I and III were noncrystalline; Procedure II gels were crystalline. No exothermic peak indicating crystallization was observed in the DTA curves for Composition 1 gels. DTA curves for Composition 2 gel samples shown in Figure 1 display exothermic peaks around 800 C due to cristobalite.

The physical appearance of heat treated monoliths at different stages of transformation is shown in Figure 2.

To determine the influence of leaching on crystallization behavior, the gel-monoliths were leached with 5N HCl for different periods and subsequently heat treated at 700 C. Crystallinity and physical appearance were compared with those obtained with the unleached samples. The results, given in Table 4, show that chemical leaching reduced the crystallization rate significantly. Samples crystallizing on heat treatment at 700 C, when leached, showed no crystallization, even at 750 C.

Discussion. - The chemistry of the gelling process and its relation to process parameters and compositions are discussed elsewhere [16]. Gels prepared by Procedures I and III were noncrystalline and remained noncrystalline on thermal treatment up to 500 C. The gels prepared by Procedure II were crystalline after drying at room temperature. In Procedure II, sodium nitrate (not as reactive as sodium methoxide or sodium acetate and insoluble in alcohol) segregates and remains in aqueous phase of wet gels but precipitates as NaNO<sub>3</sub> as the gels dry. The heat treatment at 500 C or above decomposes the nitrate, forming reactive Na<sub>2</sub>O which reacts with the polysilicic acid species to form a vitreous phase. Thus, crystallinity decreases with heat treatment.

Table 3: Heat Treatment Effects on Compositions 1 and 2.

Composition 1				Composition 2			
Thermal History (a)	Heat Treatment C	hr	Physical Appearance	Crystallinity	Heat Treatment C		Physical Appearance
					hr	hr	
Procedure I							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	72	Transparent, porous
	800	24	Ditto		350	1 25	
	800	2	"		150	72	
	800	40	"		350	1 25	
	1000	2	"		500	4	
Transparent, gray colored glass							
Procedure II							
Air dried Ditto " " " " " "	-	-	Partially crystalline due to $\text{NaNO}_3$		800	4	Transparent, porous
	800	2	Crystallinity decreases		850	4	
	800	2	Crystallinity further decreases		850	4	
	800	40	Ditto		700	1	
	1000	1	Noncrystalline		750	4	
White powder							
Ditto							
Partially sintered mass							
Ditto							
Transparent, colorless glass							
Procedure III							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure IV							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure V							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure VI							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure VII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure VIII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure IX							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure X							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XI							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XIII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XIV							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XV							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XVI							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XVII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XVIII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XIX							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XX							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXI							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXIII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXIV							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXV							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXVI							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXVII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXVIII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXIX							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXX							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXI							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXIII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXIV							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXV							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXVI							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXVII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXVIII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XXXIX							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XL							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XLI							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	
	1000	1	"		800	4	
Transparent, gray colored glass							
Procedure XLII							
Slow heat to 800 C Ditto " " " " " "	800	13	Noncrystalline		150	16	Transparent, porous
	800	24	Ditto		350	1 5	
	800	2	"		800	4	
	800	40	"		800	4	

(a) For details of drying gels up to 800 C, see Reference 16

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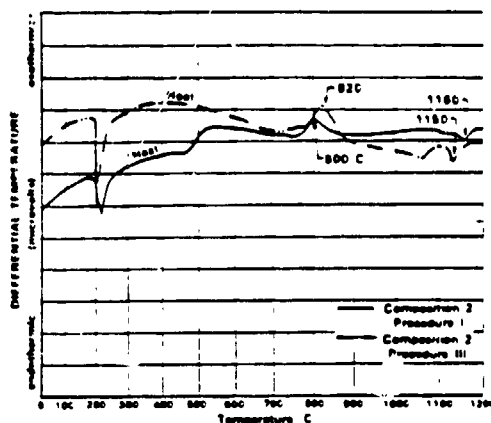


Fig. 1: DTA curves of gels after drying in air at 60 C (heating rate 10 C/min).

Our objective was to prepare a history of the vegetation in the area," McFaden says. "But these data we can also recommend as for selective cutting to a successional forest stage are today for educational purposes. Other areas can be completely as a tax forest." During the Rock Creek study, McFaden expanded on the Ca

Fig. 2: Gel-monoliths: Composition 2, Procedure I after thermal treatments above 500 C. (1) transparent noncrystalline, densified glasslike gel-monolith, (2) translucent weakly crystallized monolith, (3) opaque glass, ceramic-like monolith.

The results of the crystallization studies of the gels at temperatures higher than  $T_g$  can be summarized as follows: (a) Composition 1 gels have practically no tendency toward crystallization on heat treatment above 500 C; the gel-to-glass conversion can be achieved easily without crystallization, (b) Composition 2 gel-monoliths have a strong crystallization tendency during gel-to-glass conversion. Glass is formed on appropriate thermal treatment above 600 C, (c) crystallization rate of Composition 2 gels is controlled by the time and temperature both of heat treatment above  $T_g$  and of aging treatment at lower temperatures (e.g., 150 C), and (d) the concentration of leachable sodium ions has a strong influence on the crystallization rate.

Note that the glass of Composition 2 prepared by cooling molten oxide is much more stable toward crystallization than the porous gel-monoliths of the same composition. Several researchers [13, 14, 15, 17] report that relatively small quantities of adsorbed alkali ions on silica gel, amorphous silica powder, and silica glass-powders can cause crystallization at lower temperatures. It is suggested [9, 13, 17] that adsorbed cations enter the lattice and cause the Si-O-Si bridges to rupture, thereby collapsing the texture and lowering the crystallization temperatures. The crystallization of gels of Composition 2 is presumably due to the high reactivity of the mobile  $Na^+$  ions on the less compact gel structure and, subsequent, rupture of the Si-O-Si bonds. Hence, the mobility, (i.e., the structural state or environment) of  $Na^+$  ions in the gel structure may be an important parameter controlling the crystallization rate. The reason for the improved stability toward crystallization after prolonged low-temperature aging might be the formation of more Si-O-Si bridges and

Table 4: Influence of Leaching on the Crystallization of Composition 2 Procedure I Porous Gels.

Thermal History		Leaching Treatment	Heat Treatment		Crystallinity	Physical Appearance
C	hr					
150	16	None	700	1/2	Partially crystallized, $\beta$ -cristobalite	Opalescent to opaque
350	1.5					
500	4					
500	4	Dilute HCl, 1/2 hr at RT	700	1/2	Noncrystalline	Completely transparent, colorless
500	4	Dilute HCl, 1/2 hr at RT	750	1/2	Noncrystalline	Ditto
500	4	Dilute HCl, 16 hr at RT	700	1/2	Noncrystalline	"

compaction of gel structure at lower temperatures. The work of Brinker and Mukherjee [18] on the densification of gel-monoliths prepared by similar procedures shows the evidence of densification at lower temperatures.

The great reduction in the crystallization tendency of the porous gels on chemical leaching can be explained as follows. Presumably, there are two kinds of  $\text{Na}^+$  ions in the gel structure. The leaching treatment removes one kind of  $\text{Na}^+$  ions that are highly mobile like adsorbed ions and can enhance the crystallization rates. The residual  $\text{Na}^+$  ions after leaching might be less mobile and less effective in inducing the crystallization. The absence of crystallization tendency in Composition I gels may be a compositional effect; in this system a viscous, low-melting soda borosilicate glassy phase might form at lower temperatures.  $\text{Na}^+$  ions being structurally incorporated into this glassy phase become less reactive and mobile, consequently, the stability of the gels toward crystallization above  $T_g$  is prolonged.

4. Conclusions. The crystallization kinetics of the gels and gel monoliths during the gel-to-glass conversion are controlled by the composition, the low-temperature aging, and heat treatment conditions above  $T_g$ . Porous gel-monoliths can be transformed into transparent noncrystalline "glass" without melting by appropriate heat treatment above  $T_g$ . The removal of  $\text{Na}^+$  ions by chemical leaching reduces the crystallization rate. The rupture of Si-O-Si bonds by highly mobile  $\text{Na}^+$  ions in the less dense gel structure might be the reason for the crystallization of silica phase.

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